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**STUDIES ON THE SYNTHESIS, PROPERTIES
AND CHEMICAL MODIFICATION OF
SUPERCONDUCTING OXIDES**

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STUDIES ON THE SYNTHESIS, PROPERTIES AND CHEMICAL MODIFICATION OF SUPERCONDUCTING OXIDES

GENERAL INTRODUCTION

This thesis presents the results of the studies on synthesis, properties and chemical modification of superconducting oxides. The sol-gel method was featured aiming at the development of new process for the synthesis of the superconducting oxides. The chemical substitution of the known superconductors and transition metal oxides were carried out in order to understand the mechanism of high temperature superconductivity, modify the crystal and electronic structure of superconductors and design new superconducting materials.

In 1986, J. G. Bednorz and K. A. Müller reported anomalously high superconducting transition temperature of 30 K in the Ba-La-Cu-O oxide system (Fig. 1) [1]. This inaugurated the new era of high-temperature ceramic superconductivity. As the result of the earnest and concentrated works not only by physicists but by chemists and material scientists after that, the record of the highest T_c was surpassed in succession [2-11], as shown in Table I. The La-Ba(Sr)-Cu-O system proved superconducting close to 40 K at atmospheric pressure [6] and up to 52 K under high pressure [7]. The T_c of Y-Ba-Cu-O superconductor, 90-95 K, exceeded the boiling point of liquid nitrogen, 77 K [8]. The Bi-Sr-Ca-Cu-O and Tl-Ba-Ca-Cu-O systems with T_c in the triple-digit range of 105-125 K were reported in 1988 [9,10]. At present, the highest value

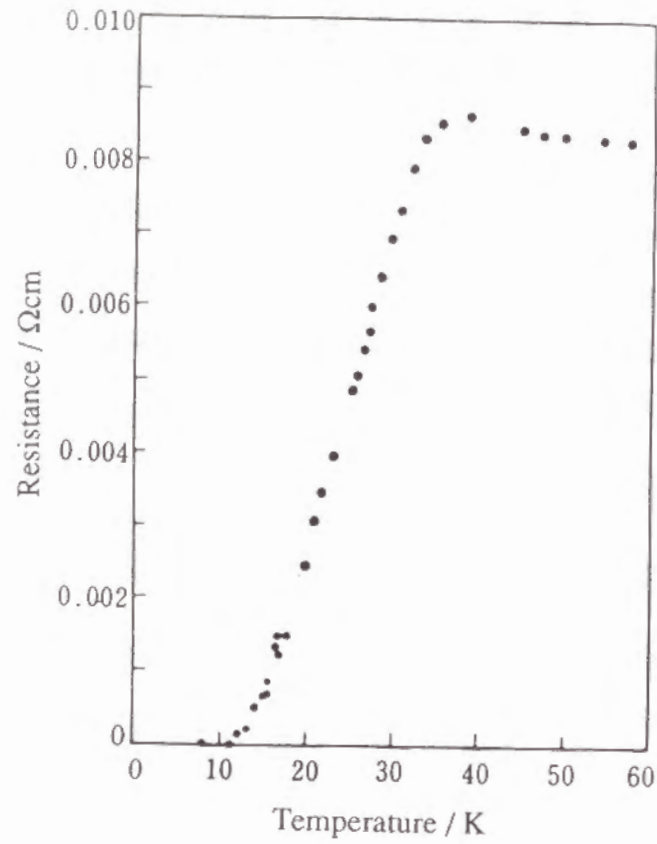


Fig. 1. The temperature-resistance curve of the Ba-La-Cu-O system reported by J. G. Bednorz and K. A. Müller in 1986.

Table I Superconducting transition temperature of the oxide superconductors.

Material	T_c / K	Year of Discovery
SrTiO ₃	0.7	1964
LiTi ₂ O ₄	12.4	1973
Ba(Pb, Bi)O ₃	13	1975
Ba _x La _{5-x} Cu ₅ O _{5(3-y)}	30-35	1986
YBa ₂ Cu ₃ O _{7-x}	90-95	1987
(Ba, K)BiO ₃	30	1988
Bi-Sr-Ca-Cu-O	105-120	1988
Tl-Ba-Ca-Cu-O	110-125	1988
Hg-Ba-Ca-Cu-O	134	1993

of T_c is 134 K, achieved in Hg-Ba-Ca-Cu-O system in 1993 [11].

A new family of copper oxide superconductors is characterized as oxygen deficient, layered perovskite-like compounds with metallic conductivity. The 40 K superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ exhibits a K_2NiF_4 -type structure made of planes of CuO_6 octahedra exclusively sharing corners, separated by (La, Sr)O layers within which La and Sr are ninefold coordinated to oxygen. The structure of 90 K superconducting $\text{YBa}_2\text{Cu}_3\text{O}_{7.8}$ is related to the perovskite type wherein two thirds of the Cu ions form corner-sharing CuO_5 pyramids connected as sheets in the a - b plane while one third of the Cu ions form one-dimensional chains of squashed square planar CuO_4 groups parallel to the b -axis. The Bi-based superconductors, represented by the general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n+1}\text{O}_{6+2n}$, also have the layered structure made of corner-sharing CuO_6 octahedra, CuO_5 pyramids or square planar CuO_4 groups, separated by Bi_2O_2 or Ca layers.

It should be noted that superconductivity in copper oxide-based systems comes of the two-dimensionality of so-called CuO_2 planes in the structure [12,13]. In order to understand the role of CuO_2 planes, it is very helpful to compare the superconducting $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with its prototype insulating La_2CuO_4 . The CuO_2 planes of La_2CuO_4 consists of copper in a Cu^{2+} state and oxygen in an O^{2-} state. The $3d_{x^2-y^2}$ orbital of Cu^{2+} is split by the effects of Coulomb repulsion, resulting in the charge transfer gap between the upper level of $\text{Cu-}3d_{x^2-y^2}$ and the $\text{O-}2p$ orbitals. In this state, $3d$ holes of opposite spin in the $\text{Cu-}3d_{x^2-y^2}$ are localized on alternating $3d^9 \text{Cu}^{2+}$ ions in an antiferromagnetic order. When La^{3+} ions are partially replaced by Sr^{2+} ions, the CuO_2 planes are doped with holes for the

charge compensation. The doping of holes reduces the DOS of both the upper $3d_{x^2-y^2}$ and $\text{O-}2p$ bands, and reconstructs a new band around the Fermi level, which is called an in-gap states [14]. In this state, the antiferromagnetic order is broken and the doped holes are delocalized, showing metallic conductivity.

Although there is a general consensus that high temperature superconductivity arises from the doped CuO_2 plane in the in-gap states, the total theory for the phenomenon of high- T_c superconductivity has not been well established. The BCS phonon-based model [15] may be applicable to the copper oxide-based systems. Several other microscopic explanation are also available, but it is not obvious if any of them is superior to BCS and provides the correct model. It is also possible that an adaptation of the BCS theory with an eclectic admixture of several mechanisms such as phonon, plasmon, exciton, and others would be required to totally account for observed behavior [16].

Synthesis of copper oxide superconductors are dealt with as a matter of ceramics, for which many synthetic techniques have been developed over a long period [17]. For the bulk superconducting materials, methods of preparation are used such as the conventional solid-state reaction, the coprecipitation or the sol-gel technique. In the solid-state reaction, the process starts from mixing and grinding compounds of the desired components such as oxides, nitrates or carbonates of Cu, La, Y, Sr, Ba, Bi or other elements. The mixture with target compositions is reacted by calcining for an extended period (10-20 h) at elevated temperatures (800-1000 °C). This process may be repeated several times with pulverizing and mixing of the partially calcined material at each step. The powder thus obtained is often pelletized and sintered for the promotion of reaction or for the measurement of properties. In the sol-gel technique [18],

the starting materials are compounds such as metal alkoxides, metal carboxylates or metal acetylacetonates, which are dissolved in organic solvents or water. The sols are formed through the hydrolysis and condensation of the starting materials or through the chelation of metal ions. The amorphous gel obtained by further condensation and/or concentration of the sol is pulverized and heated at elevated temperatures, resulting in the superconducting materials.

The superconducting properties of copper oxide-based systems are quite sensitive to the preparation process. Careful attention must be paid to such factors as the heat-treatment temperature, the partial pressure of oxygen in the heat-treatment atmosphere, the number of annealing cycles and the grain sizes of the starting materials. The oxygen content of the final product, which affects significantly superconducting properties, is the most difficult to be controlled. The quality of the products in terms of superconductivity is checked with two principal methods [19]. One is the measurement of the electrical resistance of the materials. The four probe method is generally employed to determine whether they are superconductors or not and at what temperature they transform to the superconducting state. A sharp, high T_c transition is an indicator of high quality materials. The other widely used method is the determination of the magnetic susceptibility of the materials. Good quality is indicated by a sharp, high T_c transition with both the flux exclusion and flux expulsion. This is, in a sense, a more fundamental check on quality since the value of the susceptibility far below the transition temperature is a good indicator of the fraction of the superconducting phases existing in the samples. The structures of the oxide superconductors are checked by the x-ray diffraction method. Narrow lines and the absence of peaks of impurities in the diffraction

pattern indicate a good, single-phase material.

In the present work, the synthesis and the investigation of the properties and structure of the copper oxide-based superconductors and the transition metal oxides have been carried out with a view to developing a new process of preparation, modifying the crystal and electronic structure of superconductors, designing chemically a new superconducting material and elucidating the mechanism of high- T_c superconductivity. The oxide superconductors, $\text{YBa}_2\text{Cu}_3\text{O}_7$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, have been taken up for the investigation because of the respective merits as follows. $\text{YBa}_2\text{Cu}_3\text{O}_7$ is thought to be more applicable in terms of chemical stability in the ambient atmosphere and invariable superconducting properties in a long period. $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ is a good model compound for considering the mechanism of superconductivity because of its simple structure and a variety of electrical and magnetic properties appearing on changing strontium concentration. The transition metal oxides, NdNiO_{3-y} and LaSrFeO_4 were investigated in search for new superconducting materials. The sol-gel method has been applied to the preparation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ and NdNiO_{3-y} to develop the new process for the synthesis of superconductors. Chemical modification of superconductors and transition metal oxides was carried out on the basis of the chemical substitution of $\text{YBa}_2\text{Cu}_3\text{O}_7$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, NdNiO_{3-y} and LaSrFeO_4 .

In chapter 1, the synthesis of the superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ by the sol-gel method under 1 atm oxygen pressure is described, and the mechanism of formation of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the sol-gel synthesis is presented.

In chapter 2, the effects of the chemical substitution on the structure and properties of $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconductor are described. The substitution of Sr,

K or Na for Ba and that of Li for Cu in $\text{YBa}_2\text{Cu}_3\text{O}_8$ are carried out and the results are discussed in terms of the contraction of the lattice, the formation of oxygen vacancies, the concentration of holes, the magnetic impurity effect and the role of grain boundaries.

In chapter 3, the preparation of the perovskite-type NdNiO_{3-y} by the sol-gel method under ambient pressure is described. A new oxygen-deficient phase of NdNiO_{3-y} is found and its electrical properties are discussed in terms of the changes in the lattice constants by the different oxygen content and/or the substitution of Y for Nd.

In chapter 4, the effects of the substitution of sulfur for oxygen on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor are described. The results are discussed in terms of the changes of the lattice constants, the electronic structure of the CuO_2 planes and the concentration of holes.

In chapter 5, the preparation and properties of $\text{La}_{1-x}\text{M}_x\text{SrFeO}_4$ ($\text{M}=\text{Ca}, \text{Sr}, \text{Ba}, \text{Y}$) with the K_2NiF_4 structure are described. The changes in structure and properties are discussed on the basis of the ligand field theory and the electronic transport properties of the oxides.

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CHAPTER 1

SYNTHESIS OF $\text{YBa}_2\text{Cu}_4\text{O}_8$ SUPERCONDUCTOR BY THE SOL-GEL METHOD

INTRODUCTION

The sol-gel method has been applied to the preparation of bulk, fibers and thin films of a lot of oxides which are used as electronic and optical materials for many years [1]. After the discovery of the Y-Ba-Cu-O and the Bi-Sr-Ca-Cu-O superconductors, the sol-gel method attracted much attention as the technique which enables us to produce easily the fibers and thin films of the superconductors [2-5]. On the other hand, noting that the other advantage of the sol-gel method, which is the low-temperature process, one can apply the sol-gel method to the synthesis of the different phases other than the phases usually obtained by the conventional preparation method. That is, the sol-gel method is suitable for the investigation of the low-temperature phases of the oxides, including a search for unknown phases.

In this chapter, the synthesis of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor, which is decomposed at about 800 °C in the ambient atmosphere, by the sol-gel method under 1 atm oxygen pressure is described. In Section 1, the preparation of a single-phase $\text{YBa}_2\text{Cu}_4\text{O}_8$ is attempted through the sol-gel process starting with

an aqueous solution of metal acetates and tartaric acid. In Section 2, the precise investigation of the phases evolved in the heat-treated gels are carried out, and the mechanism of the formation of the $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconducting oxide in the sol-gel process is elucidated.

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SECTION 1 PREPARATION OF SINGLE-PHASE $\text{YBa}_2\text{Cu}_4\text{O}_8$ FROM GELS

1. INTRODUCTION

The high- T_c superconductor $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) was originally found as a lattice defect in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123) powders [1] and as an ordered defect structure in the Y-123 thin films [2,3]. Karpinski *et al.* [4] prepared the bulk phase $\text{YBa}_2\text{Cu}_4\text{O}_8$ under a high oxygen pressure of 400 bar at 1040 °C. Cava *et al.* [5] succeeded in preparing this material at ambient oxygen pressure, although about 10 % of the material consisted of crystals other than $\text{YBa}_2\text{Cu}_4\text{O}_8$.

It was assumed that the Y-124 phase had a critical temperature lower than the Y-123 phase [4-6]. However, the *c*-axis-oriented faulted $\text{YBa}_2\text{Cu}_4\text{O}_8$ thin films prepared by both the electron-beam evaporation and the reactive magnetron sputtering showed the onset temperature of 96 K and zero-resistance temperature of 93 K [7]. Similar results were reported for the bulk $\text{YBa}_2\text{Cu}_4\text{O}_8$ in which Ca^{2+} was substituted for 10 % of Y^{3+} [8]. These indicate that the Y-124 phase might not be inferior to the Y-123 phase in superconducting properties. It was also reported that the oxygen content of the Y-124 phase is thermally stable up to 850 °C [4]. The most important characteristic of the Y-124 phase is its high chemical stability against moisture and carbon dioxide gas [5], which is not the case for the Y-123 phase.

The major problem encountered in the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ is the difficulty in preparing a single phase by the conventional sintering method. At higher temperatures the Y-124 phase decomposes into the Y-123 and CuO , and

below the decomposition temperature at 850 °C crystallization and sintering do not proceed well [4,5].

In order to overcome these difficulties, Kourtakis *et al.* [9] employed a spray drying method. The Y-124 powder prepared by this method from barium and yttrium acetates and copper nitrate contained 93-94 % pure powder of Y-124 phase when it was heated at 800 °C in flowing oxygen. More recently, Murakami *et al.* [10] applied the sol-gel method to the preparation of the Y-124 powders using barium and yttrium alkoxides and copper nitrate as starting materials and ethanol-xylene mixture as solvent. Mazaki *et al.* [11] used metal nitrate, citric acid, and ethylene glycol as solvent to prepare the Y-124 pellets. A pure single phase of the Y-124, however, has not been obtained by these preparation methods so far.

In this work, it has been attempted to synthesize more easily the high-purity Y-124 powders and pellets by the sol-gel method [12-15], in which only metal acetates and water containing tartaric acid are used as starting materials and no organic solvents are used [13-15].

2. EXPERIMENTAL

2.1. Preparation of the Gels

Figure 1 shows the process for synthesizing the Y-124 phase via the sol-gel method in the present work. 2.12 g of $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ (Mitsuiwa Pure Chemicals, Osaka, Japan), 3.20 g of $\text{Ba}(\text{CH}_3\text{COO})_2$ (Wako Pure Chemical Industries, Osaka, Japan), and 4.56 g of $\text{Cu}(\text{CH}_3\text{COO})_2$ (Wako Pure Chemical Industries) were dissolved in 200 ml distilled water and then the solution was stirred for 1 h at room temperature. After addition of 1.620 g of tartaric acid

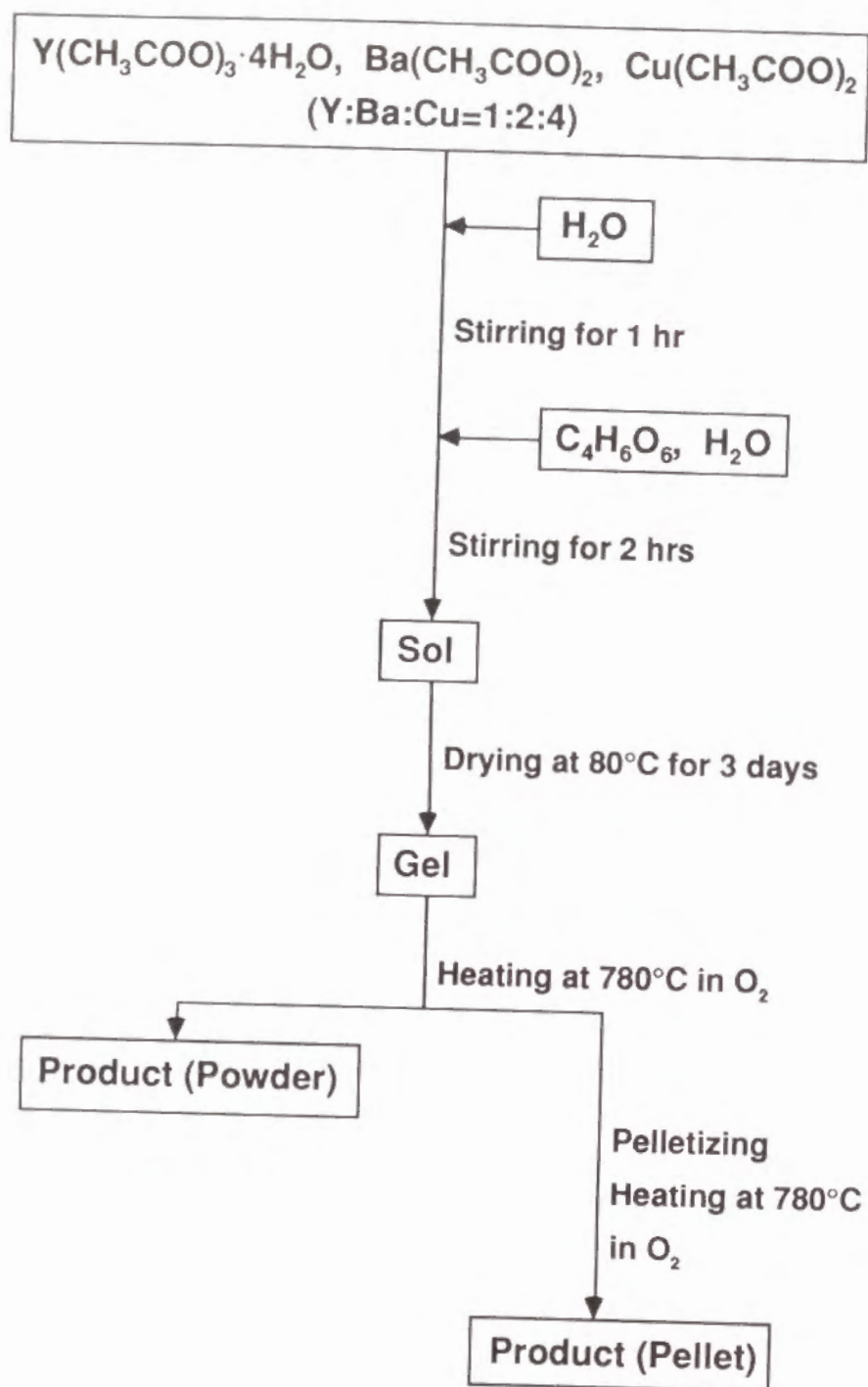


Fig. 1. The process for the synthesis of $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor via the sol-gel method.

($\text{C}_4\text{H}_6\text{O}_6$) dissolved in 10 ml distilled water, the aqueous solution was stirred for 2 h. The molar ratio of $\text{C}_4\text{H}_6\text{O}_6/\text{Cu}$ was fixed at 0.43. The resultant transparent aqueous solution with blue color was kept in a furnace at 80°C for three days to be gelled.

2.2. Heat-Treatment of the Gels

The dried gel was pulverized in an agate mortar. Two series of heat-treatments were carried out with the gel powder. In one series of heat-treatment, the gel powder was heated at temperatures from 720°C to 800°C typically for 10 h in flowing oxygen at a flow rate of 2.0 L/min and at 780°C for 10 h in air, then cooled slowly in the furnace. A heating rate of 160°C/h was adopted. In the other series of heat-treatment, the gel powder was heated at 780°C for 10 or 30 h in O_2 and then pressed into a pellet of 13 mm diameter and about 1 mm thick under a pressure of 6 MPa. The pellet was sintered at 780°C for various hours in flowing oxygen. Sintering in air was also performed.

2.3. Characterization of the Products

The crystalline phases evolved in the products after the calcination were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA diffractometer using $\text{CuK}\alpha$ radiation. The d.c. electrical resistance of the samples was measured at temperatures from 300 K to 30 K by the four-probe method. The a.c. magnetic susceptibility of the samples was measured from 300 K to 30 K by the Hartshorn bridge method with a frequency of 270 Hz and an amplitude of 100 mV, using a Chino Instrument Company superconductivity test system.

3. RESULTS

3.1. Phase Analysis

Figure 2 shows the XRD patterns of the powder products obtained by heating the gel at various temperatures for 10 h in flowing oxygen, and Table I shows the crystalline phases observed in the products. At 720 °C, BaCuO_2 , $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ [16], $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ [17], Y_2O_3 , CuO and BaCO_3 are found besides the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123). $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) appears at 760 °C and grows as the heating temperature increases to 780 °C, at which $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ and CuO remain in the sample. At 800 °C, the Y-124 and CuO are observed.

The crystalline phases observed in the powders heated at 780 °C for 5, 10, 20 and 30 h in O_2 are summarized in Table I, and the XRD patterns of the powders heated at 780 °C for 10 and 30 h in O_2 and for 10 h in air are shown in Fig. 3. The powder heated for 5 h consists of the Y-124 phase, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, $\text{Y}_2\text{Cu}_2\text{O}_5$, and CuO as shown in Table I. Besides these phases, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ appears in the sample heated for 10 h. $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ and CuO disappear and the Y-124, $\text{Y}_2\text{Cu}_2\text{O}_5$, and $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ remain on heating for 20 h. Then the Y-124 phase is obtained as a single phase on heating for 30 h. The powder obtained by heating in air at 780 °C for 10 h consists of four phases, $\text{Y}_2\text{Cu}_2\text{O}_5$, Y_2O_3 , CuO and BaCO_3 and no Y-124 phase is found.

The lattice constants of the single-phase Y-124 powder measured by the XRD are $a=0.3846$ nm, $b=0.3871$ nm and $c=2.722$ nm which are in good agreement with those of the Y-124 prepared by the other methods such as the solid-state reaction under high pressure [4] or by the flux method [5,18], as shown in Table II.

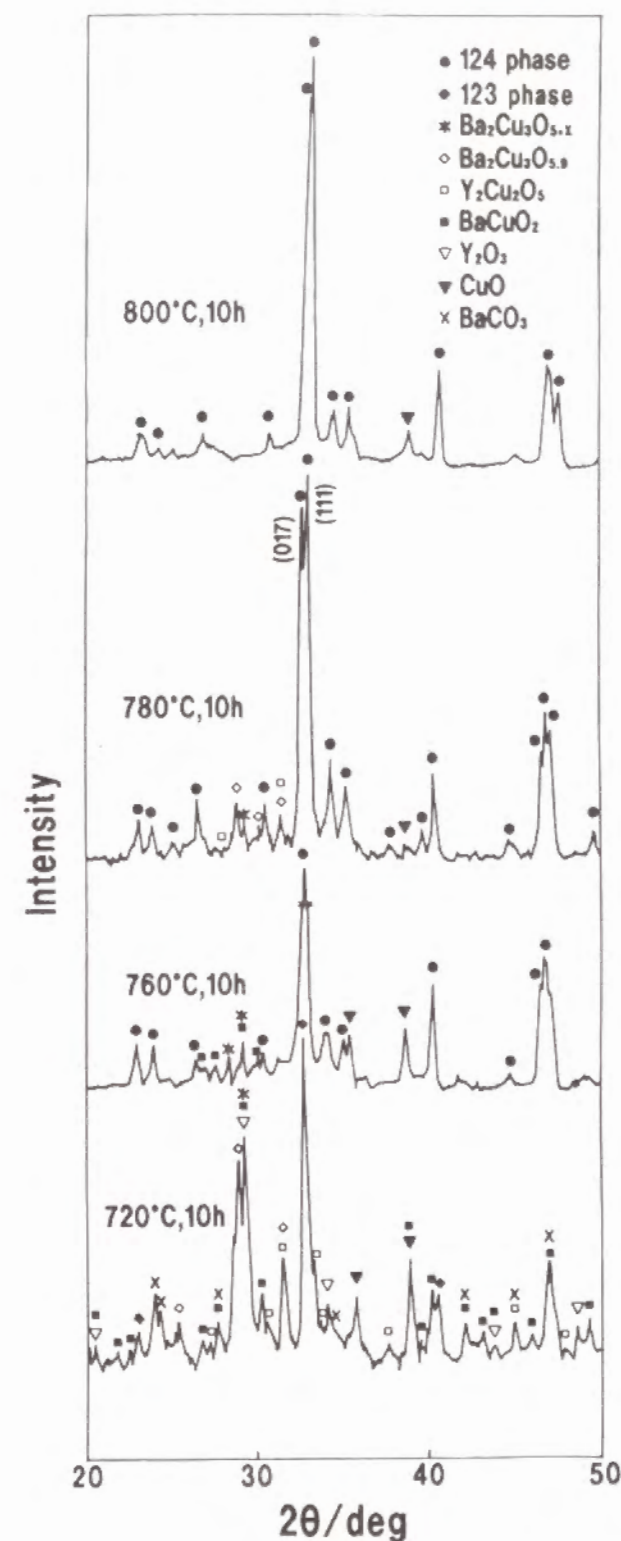


Fig. 2. The XRD patterns of powder products obtained by heating the gel at 720 - 800 °C for 10 h in flowing oxygen.

Table I Crystalline phases observed after the heat-treatment of the gel. Y-123 and Y-124 represent $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$, respectively.

Sample	Heating Condition	Crystalline Phases
Powder	720°C, 10h, O_2	Y-123, $\text{Y}_2\text{Cu}_2\text{O}_5$, BaCuO_2 , $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$, Y_2O_3 , CuO , BaCO_3
	760°C, 10h, O_2	Y-124, BaCuO_2 , $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, CuO
	800°C, 10h, O_2	Y-124, CuO
	780°C, 5h, O_2	Y-124, $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, CuO
	780°C, 10h, O_2	Y-124, $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$, CuO
	780°C, 20h, O_2	Y-124, $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$
	780°C, 30h, O_2	Y-124
	780°C, 10h, air	$\text{Y}_2\text{Cu}_2\text{O}_5$, Y_2O_3 , CuO , BaCO_3
	780°C, 10h, air	$\text{Y}_2\text{Cu}_2\text{O}_5$, Y_2O_3 , CuO , BaCO_3
Pellet	780°C, 10h, O_2	Y-124, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$
	780°C, 30h, O_2	Y-124
	780°C, 10h, air	Y-123, BaCuO_2 , CuO

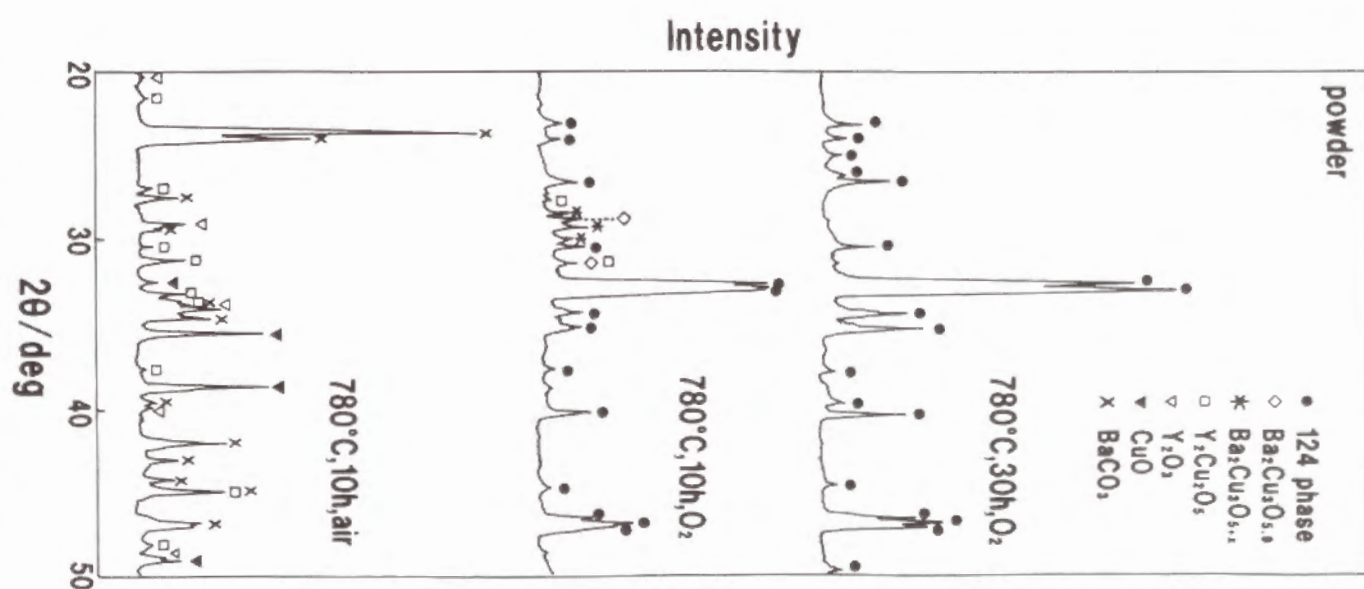


Fig. 3. The XRD patterns of powder products obtained by heating the gel at 780 °C for 10 and 30 h in flowing oxygen and for 10 h in air.

Table II Methods of the preparation and the lattice constants of $\text{YBa}_2\text{Cu}_3\text{O}_x$.

Method	Heating Condition	Lattice Constants / nm		
		<i>a</i>	<i>b</i>	<i>c</i>
Solid State Reaction [4]	400 bar O_2 , 1040°C	0.3840	0.3871	2.755
Flux Method [5]	1 atm O_2 , 800°C	0.38457	0.38711	2.7262
Flux Method [20]	1 atm O_2 , 815°C	0.3842	0.3871	2.724
Sol-Gel [this work]	1 atm O_2 , 780°C	0.3846	0.3871	2.722

Figure 4 shows the XRD patterns of the pellets sintered at 780 °C for 10 and 30 h in O_2 and for 10 h in air. Before sintering, the pellet consisted of the mixture of four phases as shown in Table I (780 °C, 10 h). After sintering for 10 h, the Y-124 phase, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ remain in the sample. The pellet sintered for 30 h consists of a single phase of Y-124 compound, and no trace of the Y-123 phase or CuO is observed. In the sample heated in air, the Y-123 phase, BaCuO_2 , and CuO are found.

3.2. Superconductivity

Figure 5 shows the temperature dependence of the a.c. magnetic susceptibility of the Y-124 powder heated at 780 °C for 10, 20 and 30 h in O_2 . The measurements were carried out for the 0.4 g of each powder sample. The samples heated for 20 and 30 h show the superconducting transition at 80 K, which is in good agreement with the value published previously [4]. The sample heated for 10 h shows the transition at 69 K and less change in susceptibility below the transition temperature. In this sample, the oxygen or copper content might deviate from the stoichiometric value because the crystallization of the Y-124 phase was not completed as seen from Fig. 3.

The powder sample of the single-phase Y-124 was pressed into pellet and sintered at 780 °C for 10 h in O_2 . Figure 6(a) shows the temperature dependence of the resistance of this pellet. The resistance decreases monotonically with decreasing temperature, starts to drop at 93 K, and becomes zero at 78 K. Two lines were extrapolated as shown in the figure to determine T_c (onset), which was found to be 87 K. The value of T_c (onset), 87 K, is slightly higher than those reported previously [4,9,18]. Figure 6(b) shows the temperature dependence of the resistivity and the susceptibility of the Y-124 pellet sintered

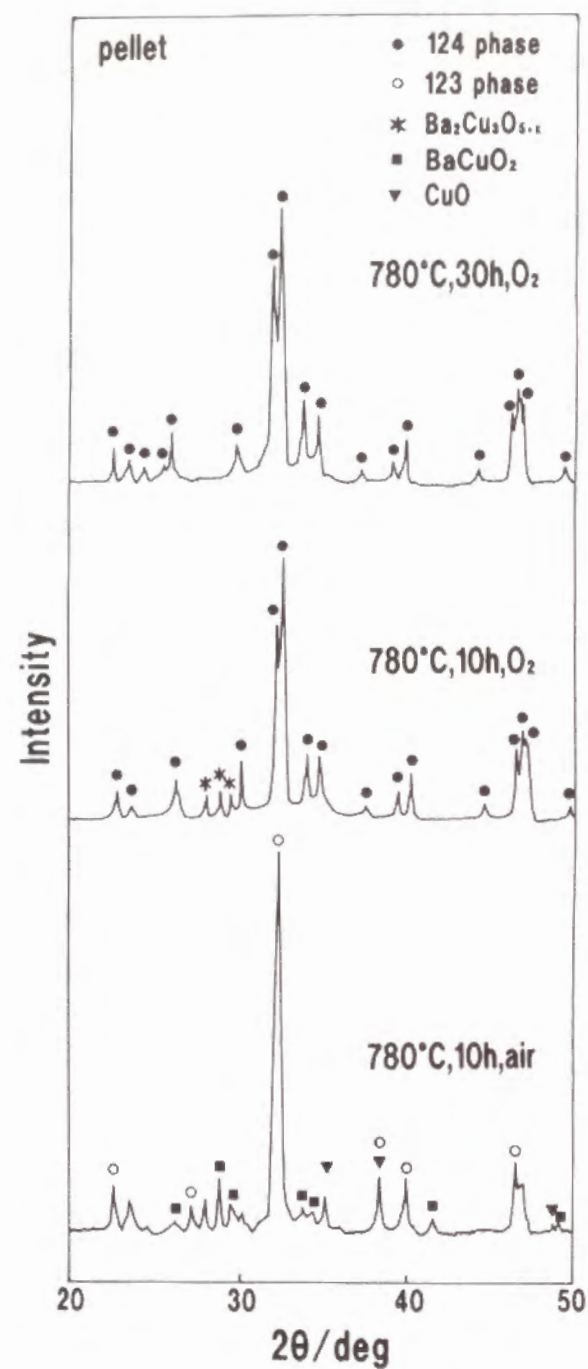


Fig. 4. The XRD patterns of the Y-124 pellets heated at 780°C for 10 and 30 h in O_2 and for 10 h in air.

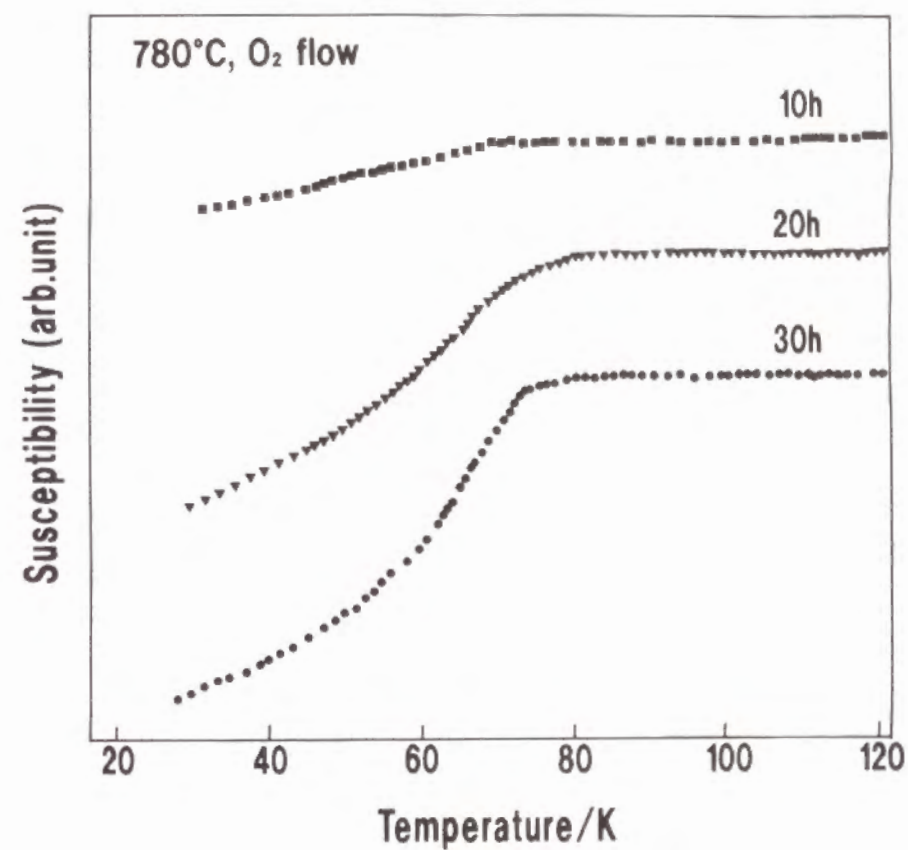


Fig. 5. Temperature dependence of the a.c. magnetic susceptibility of the Y-124 powder heated for 10, 20 and 30 h.

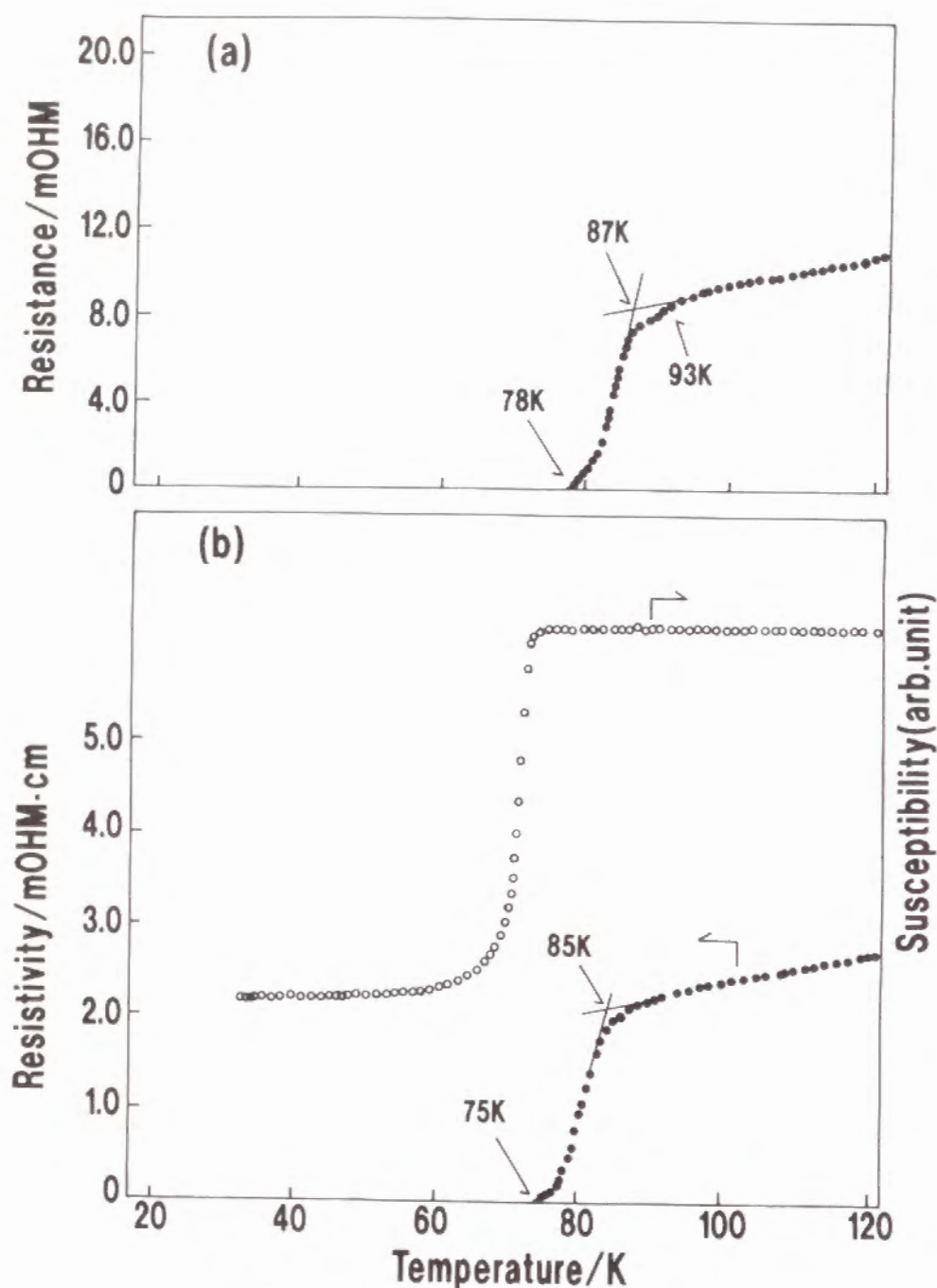


Fig. 6. (a) Temperature dependence of the electrical resistance of the pellet obtained by sintering the single-phase Y-124 powder. (b) Temperature dependence of the resistivity and the susceptibility of the Y-124 pellet sintered at 780 °C for 30 h.

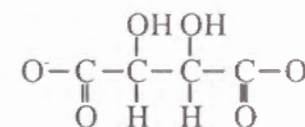
at 780 °C for 30 h in O₂ after pelletizing the powder obtained by heating at 780 °C for 10 h in O₂. The resistivity data show T_c (onset) at 85 K and T_c (end) at 75 K. The susceptibility data show $T_c(\chi)$ at 77 K and the existence of the large amount of the diamagnetic phase below T_c .

The resistivity curves shown in Fig. 6 have a so-called "foot" which makes T_c (end) lower and the transition temperature width broader. This may result from the weak link of grain boundaries of the polycrystalline phases of the Y-124 in the pellet.

4. DISCUSSION

4.1. Effect of Addition of Tartaric Acid on Formation of the Gel

A transparent gel with blue color was obtained through concentration of the aqueous solution of metal acetates and tartaric acid. Without tartaric acid, crystallization of copper acetate hydrate took place during concentration and no homogeneous gel formed. It is known that tartaric acid molecules, C₄H₆O₆, act as ligands, C₄H₄O₆²⁻ as in the following formula,



in an aqueous solution to make complexes with various metal ions [19,20]. Thus, it is assumed that copper ions and tartaric acid ligands form complexes, preventing copper ions and acetic acid ions from forming a compound which may precipitate.

4.2. Effect of Heating Temperature on Formation of the Y-124

It is known that the crystallinity of the Y-124 is well judged by the separation between (017) and (111) diffraction peaks in the XRD pattern. As seen from Fig. 2, the corresponding peak separation of the Y-124 phase produced at 780 °C is larger than that of the Y-124 produced at 760 °C and 800 °C, which indicates the better crystallinity of the sample heated at 780 °C. The diffraction peaks of CuO decrease with increasing heating temperature from 720 °C to 780 °C, and then increase at 800 °C, which may correspond to the initiation of decomposition of the Y-124. These observations indicate that the optimum temperature for the formation of the Y-124 phase is 780 °C in the present method. As seen in Fig. 3, at this heating temperature the Y-124 grows with the increase in heating time and a single phase of Y-124 is obtained when the powder is heated at 780 °C for 30 h.

4.3. Effect of Heating Atmosphere on Formation of the Y-124

Comparison between the powder sample heated at 780 °C for 10 h in flowing oxygen and that heated in air reveals that the sample heated in air has BaCO₃ and no other compounds containing Ba while the sample heated in O₂ has complex oxides of Ba such as the Y-124, Ba₂Cu₃O_{5+x}, and Ba₂Cu₃O_{5.9}. This discrepancy is explained as follows. Ba(OH)₂ formed at lower temperatures not exceeding 500 °C [21] reacts with CO₂ or carbonate ions in the gel, producing BaCO₃ during the heat-treatment [22]. At 780 °C, the resultant BaCO₃ remains stable and does not react with yttrium or copper compounds in air. On the contrary, it is assumed that BaCO₃ is less stable in the oxygen atmosphere, reacting with other compounds such as Y₂O₃, CuO and Y₂Cu₂O₅ easily at 780 °C to form Ba₂Cu₃O_{5+x}, Ba₂Cu₃O_{5.9} and the Y-124 phase.

As mentioned in 3.1., the Y-124 phase present in the pellet sample before sintering is decomposed into the Y-123 phase and CuO when it is heated in air. In any case, it can be said that heating the sample in air does not lead to the formation of the Y-124 phase.

5. CONCLUSION

A single-phase YBa₂Cu₃O₈ superconductor was obtained by heating a gel powder, which was made from the aqueous solution of metal acetates and tartaric acid, in flowing oxygen. It was found that the optimum temperature of the heat-treatment to produce the Y-124 phase was 780 °C. The powder heated at 780 °C for 30 h was a single phase of the Y-124 and showed T_c of 80 K in the susceptibility measurements, and the pellet made of this sample showed T_c (onset) at 87 K and T_c (end) at 78 K according to the resistance measurements. The other pellet sample sintered at 780 °C for 30 h consists of a pure single phase of the Y-124 with no impurity peaks observed in the XRD pattern. The resistivity measurement of this sample revealed T_c (onset) of 85 K and T_c (end) of 75 K.

Since the high-purity Y-124 powders and pellets were successfully prepared by the present technique, it is thought that the sol-gel technique is of great use when one requires the chemically modified Y-124 phase in order to investigate further its structure and properties.

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SECTION 2 FORMATION MECHANISM OF $\text{YBa}_2\text{Cu}_4\text{O}_8$ IN THE SOL-GEL SYNTHESIS

1. INTRODUCTION

The superconducting oxide $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124 phase) has been attracting much attention in view of the practical application because of stability of the oxygen content up to 850 °C [1] and high chemical stability against moisture and carbon dioxide gas [2], which is not seen in $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123 phase). The superconducting transition temperature T_c of the Y-124 phase is about 80K [1], which is *ca.* 10 K lower than that of the Y-123 phase [3], but it can be raised up to 90 K when Ca^{2+} ions are introduced into the Y-site [4].

Although there are some difficulties encountered in the synthesis of the Y-124 superconductor, the sol-gel method makes it possible to obtain a single phase of the Y-124 under the ambient pressure as described in Section 1. That is, amorphous gels were prepared from an aqueous solution of metal acetates with addition of tartaric acid, and the single-phase Y-124 ceramic powders were obtained by heating the gel at 780 °C for 30 h under 1 atm of oxygen gas [5].

Elucidation of the mechanism of formation of the Y-124 phase is essential to design and develop new and more efficient routes for preparing the Y-124 phase. In the solid-state reaction, Hurng *et al.* [6] found that nitric acid promotes the formation of $\text{Ba}_2\text{Cu}_3\text{O}_5$ from the powder mixture of Y_2O_3 , $\text{Ba}(\text{NO}_3)_2$ (or BaO or BaCO_3) and CuO, which results in the formation of the Y-124 phase in relatively short time. In the sol-gel process [5,7,8], however, it is not

clear how the Y-124 phase forms. In this section, changes of the crystalline phases precipitated in the gel were examined as a function of heating temperature and heating time, in order to clarify the chemical scheme of the gel to Y-124 phase conversion.

2. EXPERIMENTAL

2.12 g of $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, 3.20 g of $\text{Ba}(\text{CH}_3\text{COO})_2$ and 4.56 g of $\text{Cu}(\text{CH}_3\text{COO})_2$ were dissolved in 200 ml distilled water and the solution was stirred for 1 h at room temperature. 1.620 g of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) dissolved in 10 ml distilled water was added to the aqueous solution of the acetates and the solution was stirred for 2 h. The resultant transparent aqueous solution was kept at 80 °C for 3 days in order to concentrate and solidify the solution. The resultant gel was pulverized and heated at a rate of 160 °C/h to 400 °C, 500 °C, 600 °C, 700 °C and 780 °C and kept at 780 °C for 1-30 h in flowing oxygen of 1 atm.

For comparison, powder mixtures consisting of reagent grade Y_2O_3 , BaCO_3 or $\text{Ba}(\text{NO}_3)_2$ and CuO powders were pressed into pellets and heated in air or flowing oxygen of 1 atm.

Crystalline phases in the products were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA and a Rigaku Company model RINT 1200S diffractometer using $\text{CuK}\alpha$ radiation.

3. RESULTS

3.1. Formation of the Y-124 Phase in the Gel

Figure 1 shows the XRD patterns of the products obtained by heating the

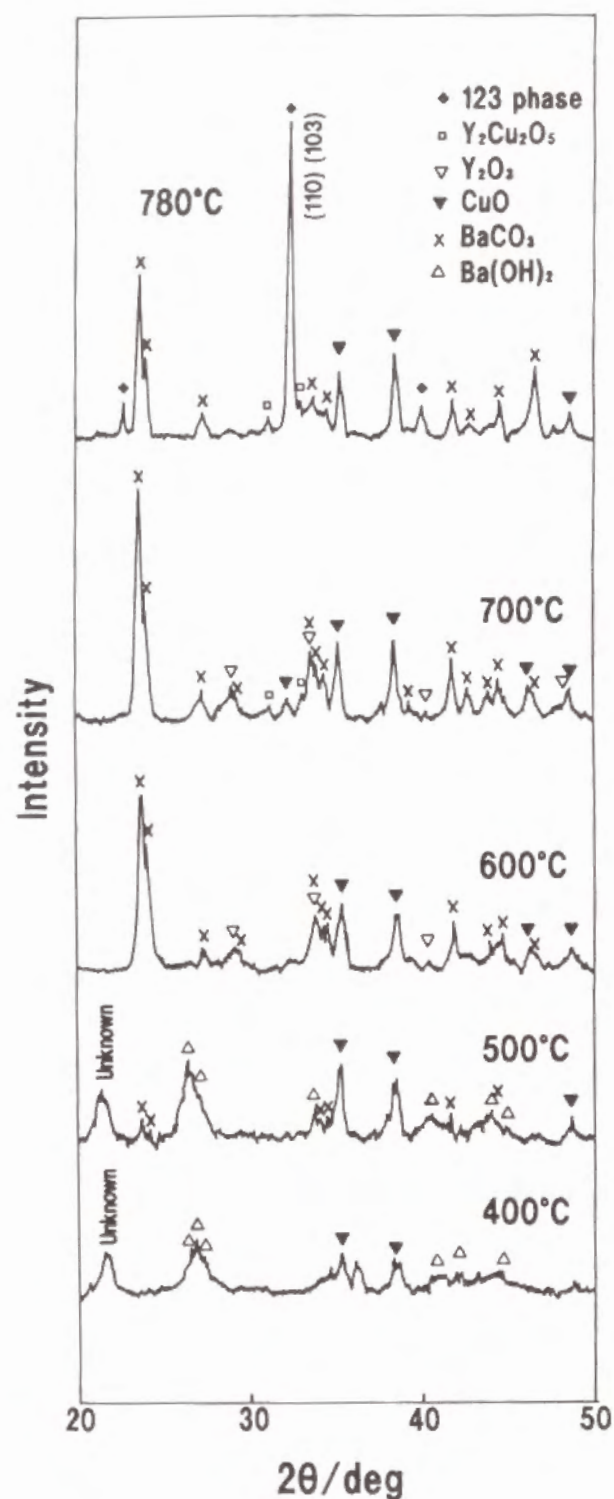


Fig. 1. The XRD patterns of the powders obtained by heating the gel to various temperatures in flowing oxygen.

gel to various temperatures in O_2 . The identified crystalline phases in these products are summarized in Table I. As can be seen in the figure and table, $Ba(OH)_2$, CuO and an unknown phase are found in the product heated to 400 °C. $BaCO_3$ starts to be formed at 500 °C, indicating that the reaction takes place between $Ba(OH)_2$ and CO_2 formed by decomposition of acetate acid anions or tartaric acid anions in the gel [9]. At 600 °C, after the transformation of $Ba(OH)_2$ to $BaCO_3$ is completed, Y_2O_3 starts to precipitate, resulting in the formation of a mixture of Y_2O_3 , $BaCO_3$ and CuO , which just correspond with the starting materials in the conventional solid-state reaction.

At 700 °C, $Y_2Cu_2O_5$ is seen besides Y_2O_3 , $BaCO_3$ and CuO (Fig. 1). Since $Y_2Cu_2O_5$ is the first complex oxide compound to precipitate, it is reasonable to assume that this compound forms *via* reaction between Y_2O_3 and CuO . In other words, $Y_2Cu_2O_5$ may be produced by the reaction (1).



Figure 2 and 3 show the XRD patterns of the products obtained by heating the gel at 780 °C for various periods of time in O_2 . The identified crystalline phases are summarized in Table I. At 780 °C, diffraction peaks of $YBa_2Cu_3O_y$ (Y-123 phase) appear. As can be seen in Fig.1 and 2, the splitting of (103) and (110) peaks of the Y-123 is not observed. This indicates that the present Y-123 phase is tetra-I phase [10-12], which is a tetragonal phase with a low oxygen defect concentration ($y=6.7-6.8$). Raising the temperature up to 780 °C results in the decrease in peak intensities of Y_2O_3 and $BaCO_3$, while those of $Y_2Cu_2O_5$ is not changed (Fig. 1). This indicates that the Y-123 phase is formed by the reaction between Y_2O_3 , $BaCO_3$ and CuO ; *i.e.* the formation of the Y-123

Table I Crystalline phases precipitated in the gel-derived powders.

Heat-Treatment	Crystalline Phases
400°C	Ba(OH) ₂ , CuO, unknown
500°C	Ba(OH) ₂ , CuO, unknown, BaCO ₃
600°C	CuO, BaCO ₃ , Y ₂ O ₃
700°C	CuO, BaCO ₃ , Y ₂ O ₃ , Y ₂ Cu ₂ O ₅
780°C	CuO, BaCO ₃ , Y ₂ Cu ₂ O ₅ , YBa ₂ Cu ₃ O _y
780°C, 1h	CuO, BaCO ₃ , Y ₂ Cu ₂ O ₅ , YBa ₂ Cu ₃ O _y
780°C, 2h	CuO, Y ₂ Cu ₂ O ₅ , YBa ₂ Cu ₃ O _y , Ba ₂ Cu ₃ O _{5+x}
780°C, 5h	CuO, Y ₂ Cu ₂ O ₅ , Ba ₂ Cu ₃ O _{5+x} , YBa₂Cu₄O₈
780°C, 10h	CuO, Y ₂ Cu ₂ O ₅ , Ba ₂ Cu ₃ O _{5+x} , Ba ₂ Cu ₃ O _{5.9} , YBa₂Cu₄O₈
780°C, 20h	Y ₂ Cu ₂ O ₅ , Ba ₂ Cu ₃ O _{5.9} , YBa₂Cu₄O₈
780°C, 30h	YBa₂Cu₄O₈

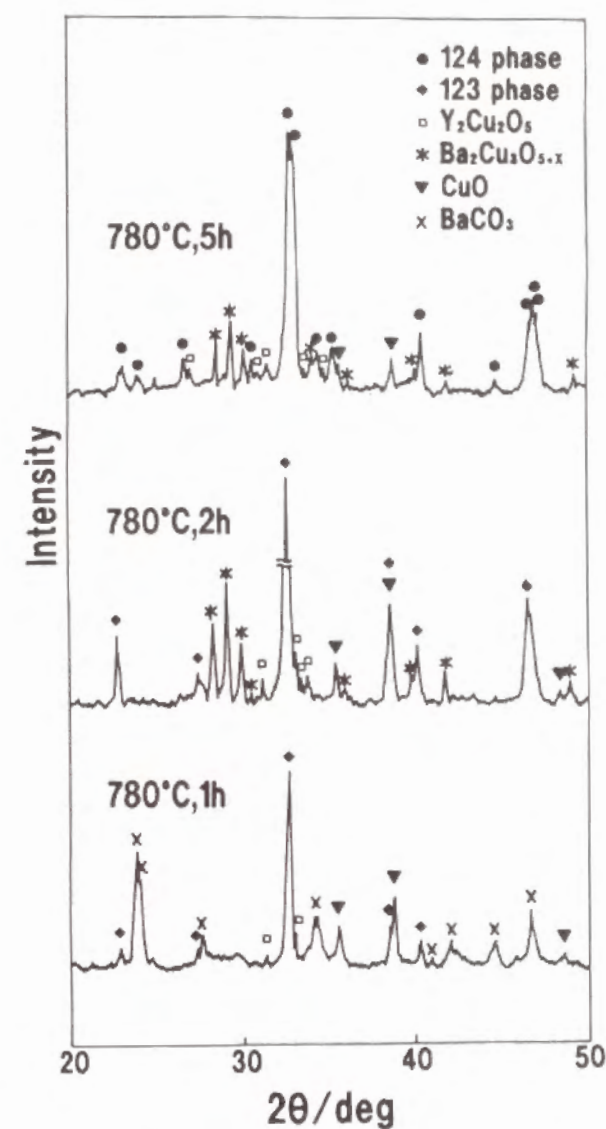


Fig. 2. The XRD patterns of the powders obtained by heating the gel at 780 °C for 1, 2 and 5 h in flowing oxygen.

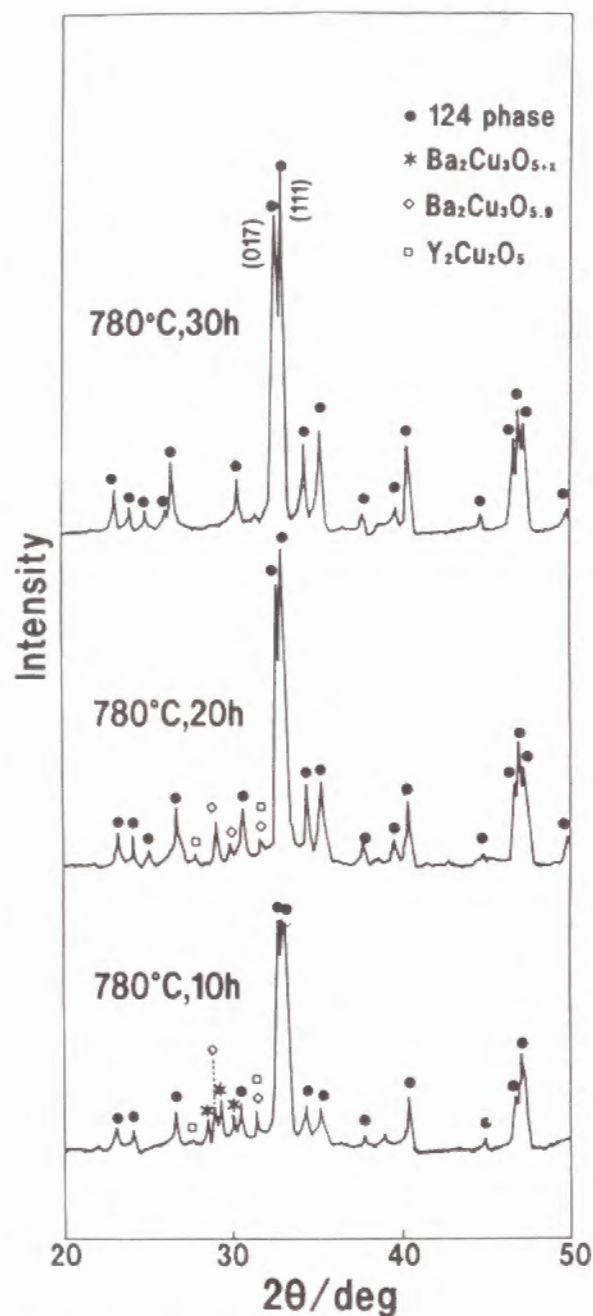
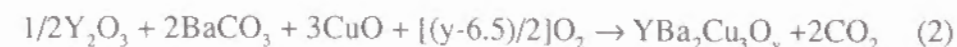
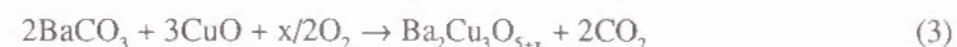


Fig. 3. The XRD patterns of the powders obtained by heating the gel at 780 °C for 10, 20 and 30 h in flowing oxygen.

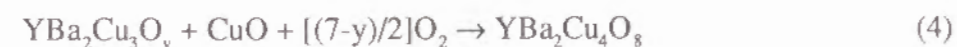
phase is assumed to follow formula (2).



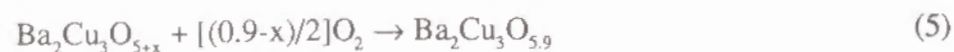
The product obtained by heating the gel at 780 °C for 2 h consists of CuO, $Y_2Cu_2O_5$, Y-123 phase (tetra-I) and $Ba_2Cu_3O_{5+x}$ (Fig. 2). It is seen that the formation of $Ba_2Cu_3O_{5+x}$ is accompanied by disappearance of $BaCO_3$. Therefore, the formation of $Ba_2Cu_3O_{5+x}$ may occur *via* reaction between $BaCO_3$ and CuO represented by formula (3).



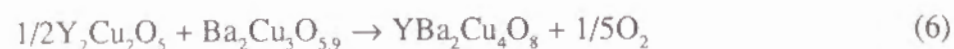
The Y-124 phase appears at the sacrifice of the Y-123 when the gel is heated at 780 °C for 5 h (Fig. 2). The splitting of the (017) and (111) peaks of the Y-124 increases with increasing heating time, followed by the decrease in intensity of CuO peaks. These indicate that the Y-123 and CuO react to form the Y-124 phase;



The XRD patterns of the products obtained by heating at 780 °C for 5, 10 and 20 h (Fig. 3) show that $Ba_2Cu_3O_{5+x}$ is transformed into $Ba_2Cu_3O_{5.9}$, which is completed by the heat-treatment for 20 h. This process may take place *via* incorporation of oxygen into $Ba_2Cu_3O_{5+x}$, which can be represented by formula (5).



The gel heated at 780 °C for 20 h consists of the Y-124 phase, $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$. Heating at 780 °C for 30 h results in disappearance of the latter two compounds and at the same time formation of the single-phase Y-124 compound (Fig. 3), indicating that $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ react to form Y-124 phase as expressed by formula (6).



3.2. Solid-State Reaction between Y_2O_3 , BaCO_3 and CuO Powders

Y_2O_3 , BaCO_3 and CuO powders with a nominal composition of Y:Ba:Cu=1:2:4 were mixed, pressed into a pellet and heated at 780 °C for 30 h in flowing O_2 of 1 atm, aiming at the formation of the Y-124 phase. Figure 4 shows the XRD pattern of the product. Although the formation of $\text{YBa}_2\text{Cu}_3\text{O}_y$, $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ and BaCuO_2 is seen, no trace of the Y-124 phase is observed in the pattern.

3.3. Formation of the Y-124 Phase from a $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ Mixture

$\text{Y}_2\text{Cu}_2\text{O}_5$ was prepared from a Y_2O_3 and CuO powder mixture by heating at 875 °C for 20 h in air. A single-phase $\text{Y}_2\text{Cu}_2\text{O}_5$ could be obtained without any impurities. $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ was prepared from a $\text{Ba}(\text{NO}_3)_2$ and CuO powder mixture by heating at 800 °C for 10 h in air. Figure 5 shows the XRD pattern of the Ba-Cu-O product. It is seen that the product consists of $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ with a trace of BaCO_3 and CuO .

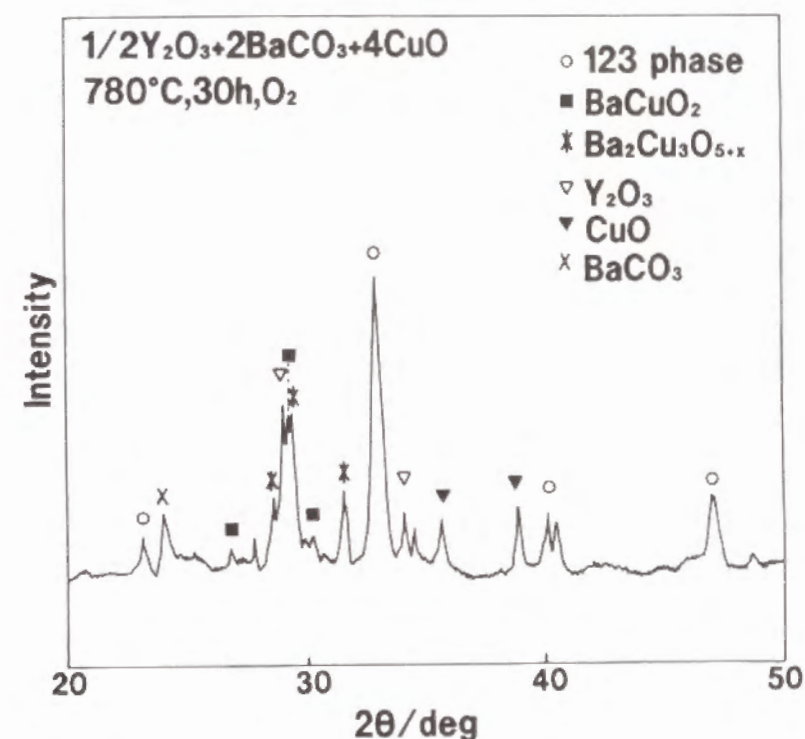


Fig. 4. The XRD pattern of the product obtained by heating the powder mixture of Y_2O_3 , BaCO_3 and CuO (Y:Ba:Cu=1:2:4) at 780 °C for 30 h in O_2 .

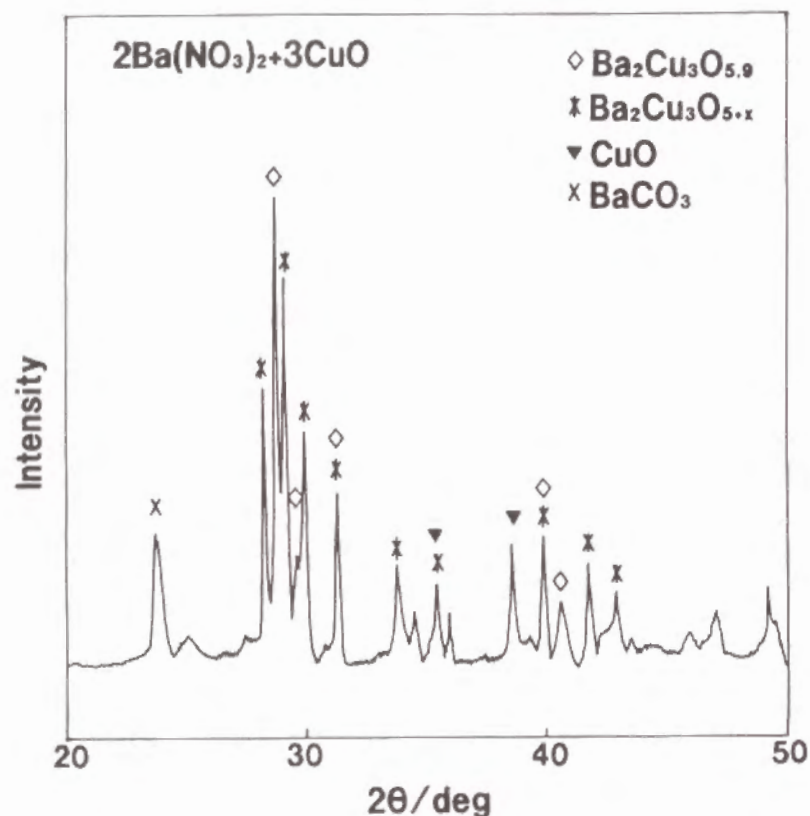


Fig. 5. The XRD pattern of the product obtained by heating the powder mixture of $\text{Ba}(\text{NO}_3)_2$ and CuO (Ba:Cu=2:3) at 800°C for 10 h in air.

$\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$ products thus obtained were ground and mixed to make a powder mixture with a nominal composition of the Y-124 phase, and pressed into a pellet. The pellet was heated at 780°C in flowing O_2 of 1 atm for 20 or 50 h. Figure 6 shows the XRD pattern of the products. Formation of the Y-124 phase is observed in the product obtained by heating for 20 h, and the amount of the Y-124 phase increases when the mixture is heated for 50 h. Formation of the Y-124 phase is accompanied with decreases in the amount of $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$. It should be noted that the decreasing rate is larger in the former than in the latter, as can be clearly seen by comparing the diffraction pattern of Fig. 6 with that of the Ba-Cu-O product in Fig. 5.

4. DISCUSSION

4.1. Formation of the Y-124 Phase from the Gels

Rapid formation of the Y-124 phase from the gel under 1 atm oxygen was clearly seen in the present study; heating the gel at 780°C for 30 h resulted in a single-phase Y-124 compound.

The formation process of the Y-124 phase from the gel, which was described in 3.1, indicates that two reaction processes expressed by formulae (4) and (6) are the key processes which lead to the formation of the Y-124 phase. One is the reaction between the tetra-I Y-123 phase and CuO (formula (4)), which includes oxidation process. Noting that the tetra-I $\text{YBa}_2\text{Cu}_3\text{O}_y$ is a highly oxidized phase whose y value is close to 7, it is expected that reaction (4) can easily proceed even when ambient oxygen pressure is not very high. In other words, formation of the highly oxidized Y-123 phase as the intermediate facilitates the conversion of the mixture of the Y-123 phase and CuO into the

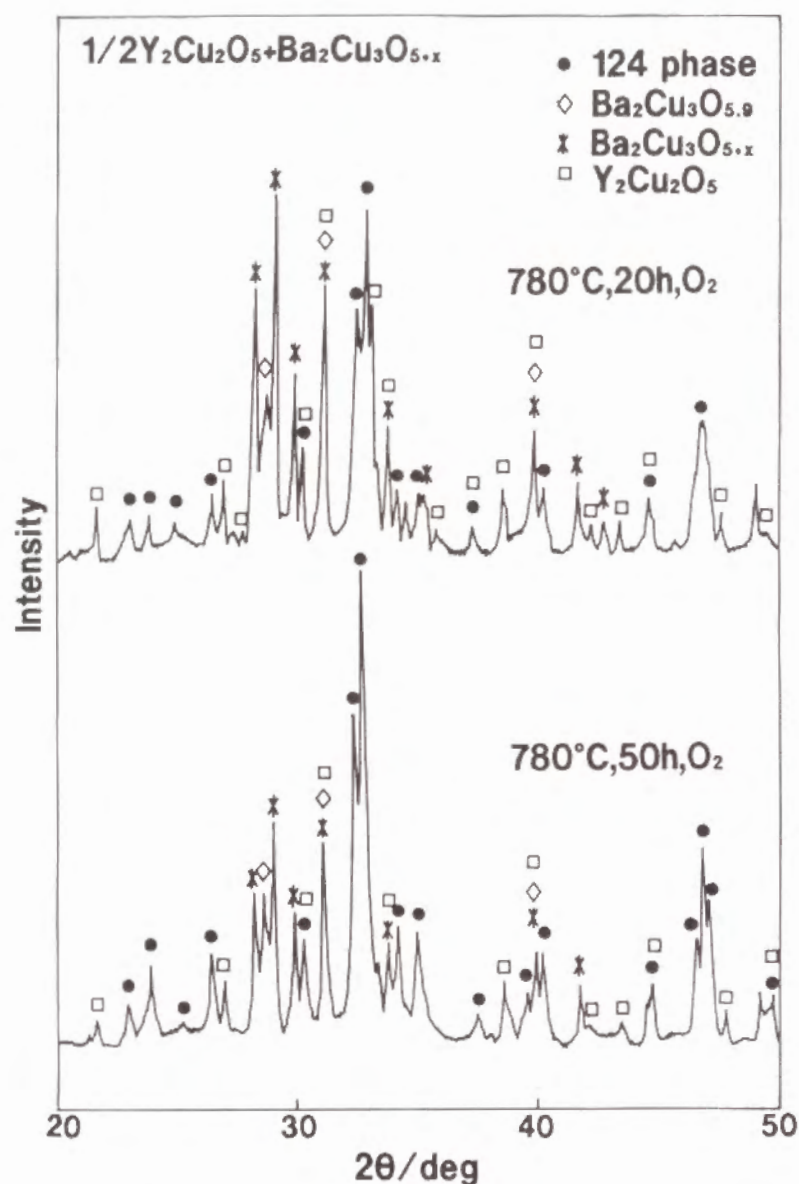


Fig. 6. The XRD patterns of the pellets obtained by heating the powder mixture of $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5+x}$ products at $780^\circ C$ for 30 and 50 h in O_2 .

Y-124 phase under 1 atm O_2 pressure.

The other process leading to the formation of the Y-124 phase from the gel is the reaction between $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5.9}$ (formula (6)). It is thought that this reaction does not need high oxygen pressure because it includes no oxidation process, which is completed at earlier stage; that is, $Ba_2Cu_3O_{5+x}$ is oxidized to $Ba_2Cu_3O_{5.9}$ as indicated by formula (5). It can be said that the formation of highly oxidized intermediate, $Ba_2Cu_3O_{5.9}$, makes it possible to prepare the Y-124 phase under 1 atm.

4.2. Formation of the Y-124 Phase through the Conventional Solid-State

Reaction

In contrast to the sol-gel synthesis, no trace of the Y-124 phase was found in the product from the powder mixture of Y_2O_3 , $BaCO_3$ and CuO . This is attributed to the low heat-treatment temperature and the large particle size of the starting materials as will be discussed in 4.3.

It has been shown in the present study that the reaction between $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5.9}$ prepared by the conventional solid-state reaction allows the formation of the Y-124 phase in a relatively high yield (Fig. 6), which verifies that the formula (6) in the sol-gel synthesis is valid. In addition, this solid-state reaction study has shown that in the formation of the Y-124 phase more highly oxidized $Ba_2Cu_3O_{5.9}$ is preferable to less oxidized $Ba_2Cu_3O_{5+x}$.

4.3. Comparison between the Sol-Gel Route and the Solid-State Reaction

Route

In the preparation of the Y-124 phase under a low pressure of 1 atm, it is indispensable to obtain the highly oxidized intermediates. It should be noted

that the highly oxidized tetra-I phase is one of the low-temperature phases [10] of the Y-123 phase, which cannot be easily synthesized from a powder mixture of oxides and carbonates through the conventional solid-state reaction because of the too low rate of reaction at low temperatures around 800 °C. Even if the heat-treatment temperature is raised to accelerate the solid-state reaction, the tetra-II Y-123, a tetragonal Y-123 phase with high oxygen defect concentration, results and the tetra-I Y-123 phase cannot be obtained.

In contrast, the tetra-I Y-123 phase is known to be formed in the ambient atmosphere when one uses amorphous precursors like gels in which constituent metal cations are homogeneously distributed [10,13]. Manthiram and Goodenough [10] prepared the tetra-I phase from metal citrate gels with the Y-123 composition at 780 °C, and Sakka *et al.* [13] reported the formation of this phase from metal acetate gels with the Y-123 composition at 800 °C. It was also observed in the present study that the tetra-I phase is formed *via* the reaction between Y_2O_3 , $BaCO_3$ and CuO which all are precipitated in the gels. The formation of the tetra-I phase is attributed to much smaller sizes and much more well-mixed state of Y_2O_3 , $BaCO_3$ and CuO in the gels than in the powder mixture used in the conventional solid-state reaction. In fact, the size of the CuO and $BaCO_3$ particles precipitated in the gel at 780 °C was as small as 20 nm as evaluated from the half-height width of the diffraction peak.

It has been confirmed that the reaction between $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5.9}$ proceeds both in the sol-gel route and in the solid-state reaction route. However, the rate of reaction between $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5.9}$ was found to be much larger in the sol-gel route than in the solid-state reaction route. This unambiguously results from the smaller size and more well-mixed state of these particles. The formation of $Ba_2Cu_3O_{5+x}$ also proceeded more rapidly in the sol-gel route, probably

because of the smaller size of the CuO and $BaCO_3$ particles. The highly oxidized $Ba_2Cu_3O_{5.9}$, which was found to be a crucial intermediate compound for the formation of Y-124 phase, is known to be a low temperature form of $Ba_2Cu_3O_{5+x}$, which is thermodynamically stable under 1 atm O_2 at temperatures lower than 900 °C [14,15]. More rapid transformation of the metastable $Ba_2Cu_3O_{5+x}$ to stable $Ba_2Cu_3O_{5.9}$ as found in the sol-gel route may result from the smaller size of the particles, which can enhance the reactivity.

5. CONCLUSION

The mechanism of the formation of $YBa_2Cu_4O_8$ from the acetate-derived gel was investigated. It was shown that there are two key routes for the formation of the Y-124 phase; one is the reaction between the tetra-I Y-123 phase and CuO, and the other the reaction between $Y_2Cu_2O_5$ and $Ba_2Cu_3O_{5.9}$. It was concluded that the formation of the tetra-I phase Y-123, which cannot be prepared by the conventional solid-state reaction under the ambient pressure, and the rapid formation of highly oxidized $Ba_2Cu_3O_{5.9}$ enable the formation of the Y-124 phase at a low oxygen pressure of 1 atm and a low temperature around 780 °C.

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CHAPTER 2

EFFECTS OF CHEMICAL SUBSTITUTION ON THE STRUCTURE AND PROPERTIES OF $\text{YBa}_2\text{Cu}_4\text{O}_8$ SUPERCONDUCTOR

INTRODUCTION

The $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor contains a group III A ion, Y^{3+} , an alkaline earth ion, Ba^{2+} , copper and oxygen. An important question that arises concerns which of the constituent ions are essential and which can be replaced by related or not so related ions. Moreover, it is interesting to know how the structure and properties of superconducting oxides change by the replacement of different ions. In many cases, new materials in oxide superconductors have been found by means of such chemical substitutions.

In this chapter, chemical substitution of $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor are discussed. In Section 1, the effects of the substitution of Sr, K or Na for Ba on the structure and properties are discussed. In Section 2, the effects of substituents in the CuO_2 planes on the superconductivity are discussed on the basis of the substitution of Li for Cu.

SECTION 1 EFFECTS OF SUBSTITUTION OF Sr, K OR Na FOR Ba ON THE STRUCTURE AND PROPERTIES OF $\text{YBa}_2\text{Cu}_4\text{O}_8$

1. INTRODUCTION

In the Y-Ba-Cu-O oxide system, there are two important superconducting phases, $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123) and $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124), which differ in the number of CuO chains in the structure as shown in Fig. 1 [1-3]. The Y-123 phase has single CuO chains and its oxygen content depends on the conditions of preparation such as the heat-treatment temperature, the partial oxygen pressure in the heat-treatment atmosphere and the cooling rate. Superconducting transition temperature T_c of the Y-123 phase decreases from 90 K as the oxygen content decreases. On the other hand, the Y-124 phase has double CuO chains and its oxygen content is almost constant up to 850 °C. T_c of the Y-124 phase is about 80 K [4], which is hardly affected by the preparation conditions.

It is known that the application of high pressure during the measurement affects T_c of the Y-124 phase much more markedly than that of the Y-123 phase. Bucher *et al.* [5] first reported that T_c of the Y-124 phase increases with pressure, p , at a rate of $dT_c/dp=5.5$ K/GPa. Yamada *et al.* [6] also reported the same value of dT_c/dp in the Y-124 phase. They attributed this effect to redistribution of holes induced by pressure. Nelmes *et al.* [7] determined the crystal structure of the Y-124 phase under pressures up to 5 GPa and suggested that the reduction of the Cu(2)-O(1) distance (see Fig. 1), namely, the distance between the copper in the CuO_2 planes and the apical oxygen, with pressure

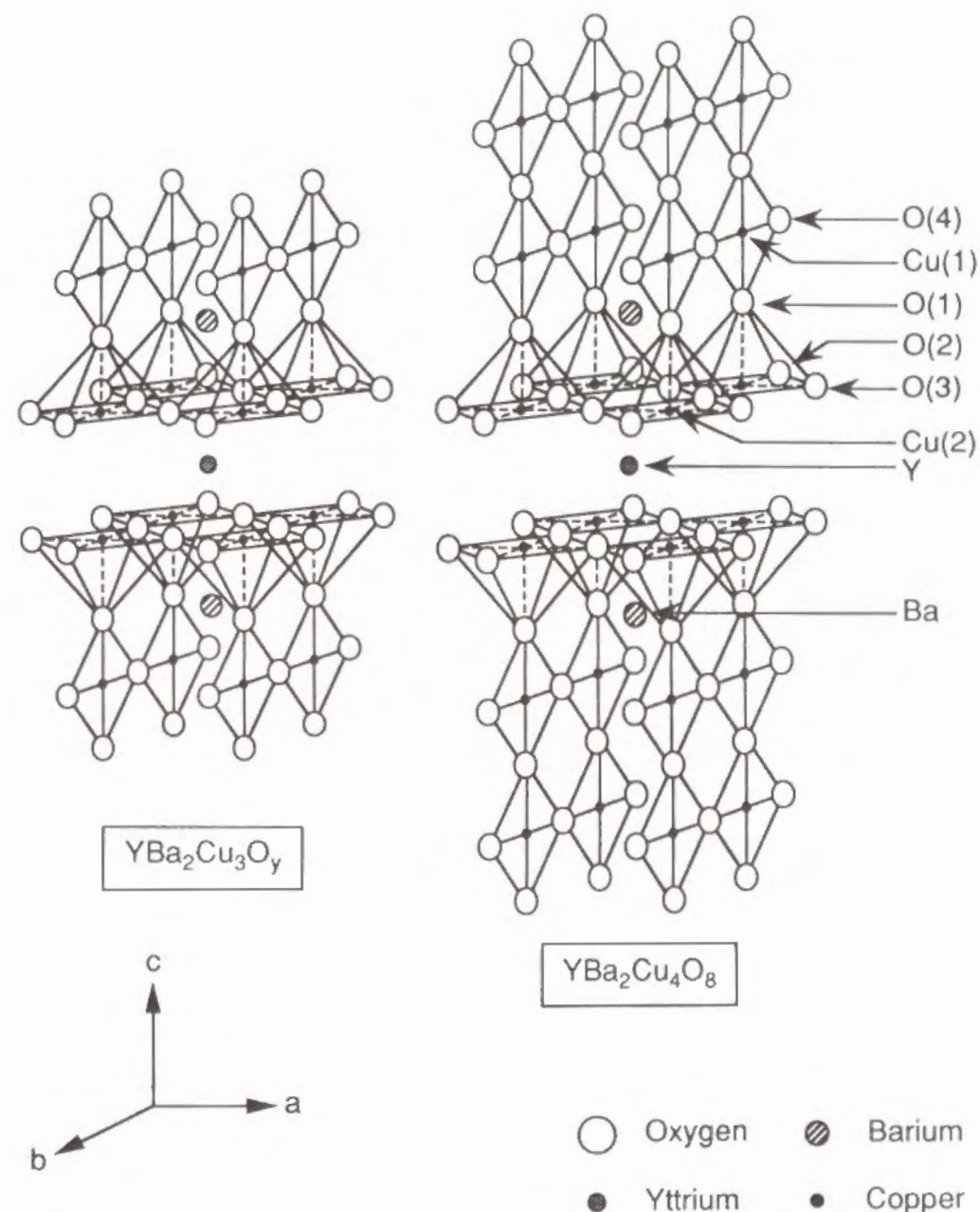


Fig. 1. Crystal structure of $\text{YBa}_2\text{Cu}_3\text{O}_y$ and $\text{YBa}_2\text{Cu}_4\text{O}_8$.

gives rise to increase in T_c by the charge transfer mechanism. This suggests that the chemical substitution, such as substitution of Sr^{2+} for Ba^{2+} , that causes contraction of the lattice of the Y-124 phase along the c -axis might shorten the Cu(2)-O(1) distance and, accordingly, increase T_c of the Y-124 phase.

Miyatake *et al.* [8] have shown that substitution of Ca for 10% of Y in the Y-124 phase raises T_c up to 90 K. They attributed the increase in T_c to the increase in the hole concentration in the CuO_2 planes. It would be interesting to know if there is a similar effect when monovalent cations are substituted for Ba^{2+} .

It is generally known that the synthesis of the Y-124 phase by solid-state reaction requires a high oxygen pressure of 400 bar and a high temperature of 1040 °C [4]. Flux method [9], spray drying [10] or sol-gel technique [11], however, have recently been shown to enable the formation of the Y-124 phase under 1 atm oxygen at temperatures lower than 800 °C. A single-phase Y-124, in fact, can be prepared by heating metal acetate-derived gels at 780 °C under 1 atm oxygen [12,13], as described in Chapter 1. This suggests that the sol-gel technique has great advantage in preparing a single Y-124 phase with partially substituted elements.

In this section, attempts were made to prepare $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$ ($\text{R}=\text{Sr}$, K or Na) by the sol-gel method and examine the changes in the lattice constants, the oxygen content, the hole concentration, T_c , and the microstructure with the Ba-site substitution. Replacement of Ba^{2+} by Sr^{2+} , which has a smaller ionic radius than Ba^{2+} , was expected to shorten the lattice constant c . Replacement of Ba^{2+} by K^+ , which has a lower valence and a similar ionic radius, was expected to increase the hole concentration. Replacement of Ba^{2+} by Na^+ , which has a smaller ionic radius and a lower valence, was expected to have both

effects.

2. EXPERIMENTAL

2.1. Sample Preparation

Metal acetates $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ (Mitsuwa Pure Chemicals, Osaka, Japan), $\text{Ba}(\text{CH}_3\text{COO})_2$ (Wako Pure Chemical Industries, Osaka, Japan), $\text{Sr}(\text{CH}_3\text{COO})_2 \cdot 0.5\text{H}_2\text{O}$ (Wako Pure Chemical Industries), CH_3COOK (Nacalai Tesque, Kyoto, Japan), $\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$ (Nacalai Tesque) and $\text{Cu}(\text{CH}_3\text{COO})_2$ (Wako Pure Chemical Industries) were used as starting materials. Pertinent amounts of metal acetates were dissolved in ion-exchanged water to make an aqueous solution with cation molar ratio of $\text{Y}:\text{Ba}:\text{R}:\text{Cu}=1:(2-x):x:4$ ($\text{R}=\text{Sr}$, K, Na; $x=0 - 0.6$). After stirring for 1 h, an aqueous solution of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) was added and the solution was stirred for another 2 h. The molar ratio of tartaric acid to copper was fixed at $\text{C}_4\text{H}_6\text{O}_6/\text{Cu}=0.43$. The resultant transparent solution was concentrated at 80 °C in an oven, and a dried gel with blue color was obtained in three days. The gel was pulverized, heated to 780 °C at a rate of 160 °C/h in flowing oxygen, kept there for 10 h and cooled in the furnace. The resultant powder with black color was ground and heated at 780 °C in flowing oxygen for other 40 h with intermittent grinding every 10 h. The resultant powder products were pressed into pellets and sintered at 780 °C for 10 h in flowing oxygen for the electrical resistance measurements.

2.2. X-Ray Analysis

The crystalline phases in the product were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA

diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the Y-124 phase were determined by XRD using Si as the internal standard substance. The d values were calculated from the measured 2θ values using the least square method.

2.3. Iodometric Titration

The oxygen contents of the products were determined by an iodometric titration technique, as shown in Fig. 2. First, for the determination of the total copper content in the product, the exactly weighed powder product (W_1 g) was dissolved in 1 N HCl, and KI and a buffer solution consisting of ammonium acetate and acetic acid were added to the solution. The resultant solution was titrated with a N/100 $\text{Na}_2\text{S}_2\text{O}_3$ standard solution (V_1 l) using an aqueous solution of starch as an indicator, while the solution was purged with N_2 gas. For the determination of the valence of copper represented by Cu^{2+p} , the exactly weighed powder product (W_2 g) was dissolved in 1N HCl solution to which KI was beforehand added, followed by an addition of the buffer solution. The resultant solution was titrated with the N/100 $\text{Na}_2\text{S}_2\text{O}_3$ standard solution (V_2 l). The formal charge of copper, $2+p$, was determined from the following equation;

$$p = (V_2/W_2)/(V_1/W_1) - 1.$$

The oxygen content was calculated taking into account the balance of the positive and negative charge of the constituent ions in $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$.

2.4. Flame Spectrometrical Analysis

The potassium content in the product was determined by a flame

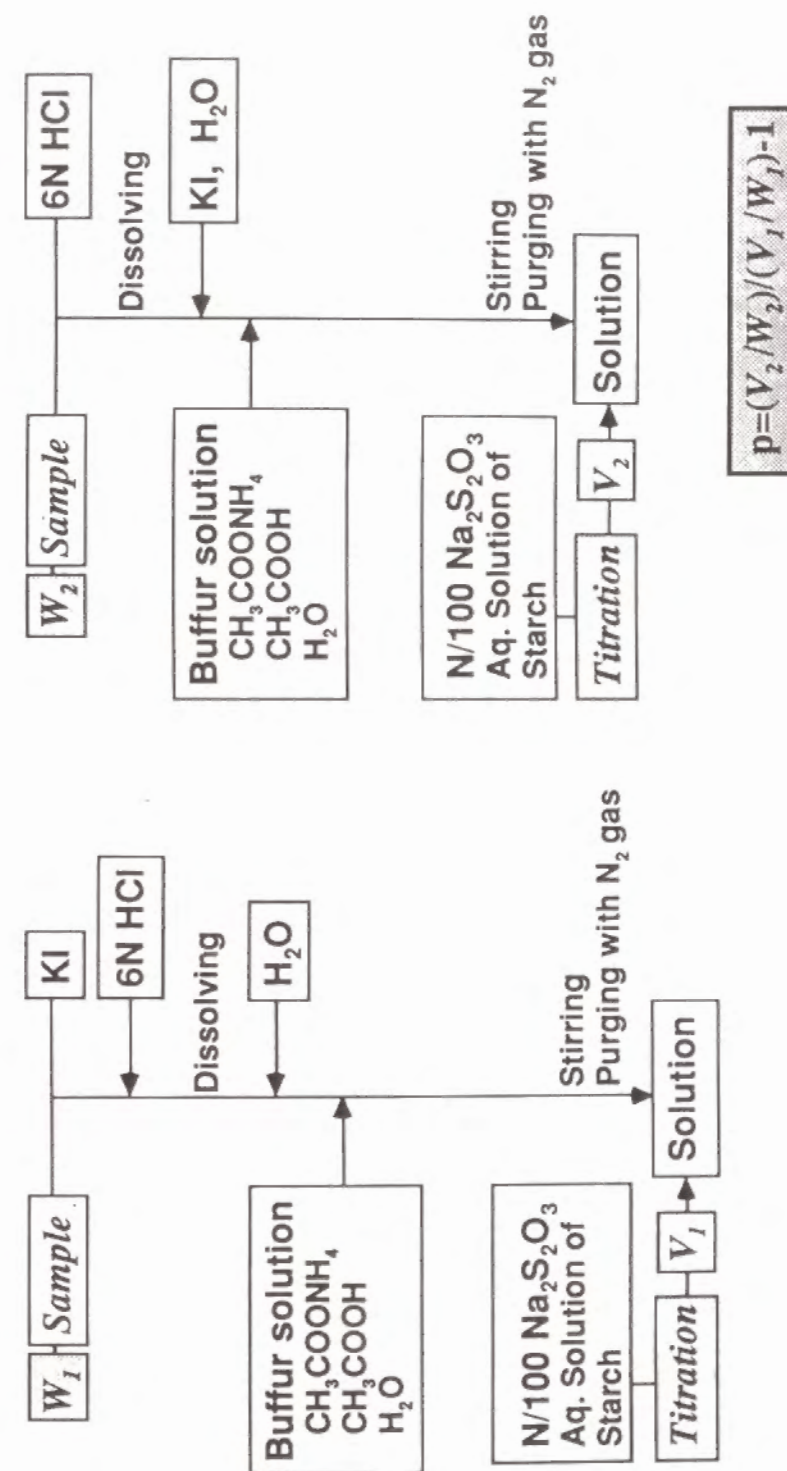


Fig. 2. The schematic diagram of the iodometric titration for the determination of the copper valence, Cu^{2+p} .

spectrometrical analysis. The K-containing product was dissolved in 1 N HCl and diluted to make a solution with K^+ concentration of 0.1-1.0 ppm. The solution was analyzed by a spectrometrical method with a Seiko Instrument Company model SAS-727 atomic absorption spectrophotometer. The exact concentration of K^+ in the solution was determined from a calibration curve which was obtained using standard solutions of K^+ with concentrations of 0.1, 0.4, 0.7 and 1.0 ppm.

2.5. Electrical Resistance

The d.c. electrical resistance of the sintered pellets was measured at temperatures from 300 K to 30 K by a four probe method with a Chino Instrument Company superconductivity test system. The cooling rate was fixed at 17 K/h.

2.6. SEM Observation

The microstructure of the sintered pellets was observed with a Hitachi model S-450 scanning electron microscope (SEM).

3. RESULTS

3.1. Formation of $YBa_{2-x}Sr_xCu_3O_8$

The formation of the substituted Y-124 crystalline products took place through the crystallization process similar to that for the formation of the non-substituted $YBa_2Cu_3O_8$, which was described in Chapter 1. Figure 3 shows the XRD patterns of the powder products obtained by heating the gel with a composition of $YBa_{1.8}Sr_{0.2}Cu_4O_8$ for 10, 30 and 50 h in flowing oxygen. CuO , $Y_2Cu_2O_5$, $Ba_2Cu_3O_{5+x}$ and $Ba_2Cu_3O_{5.9}$ remain in the sample in addition to the

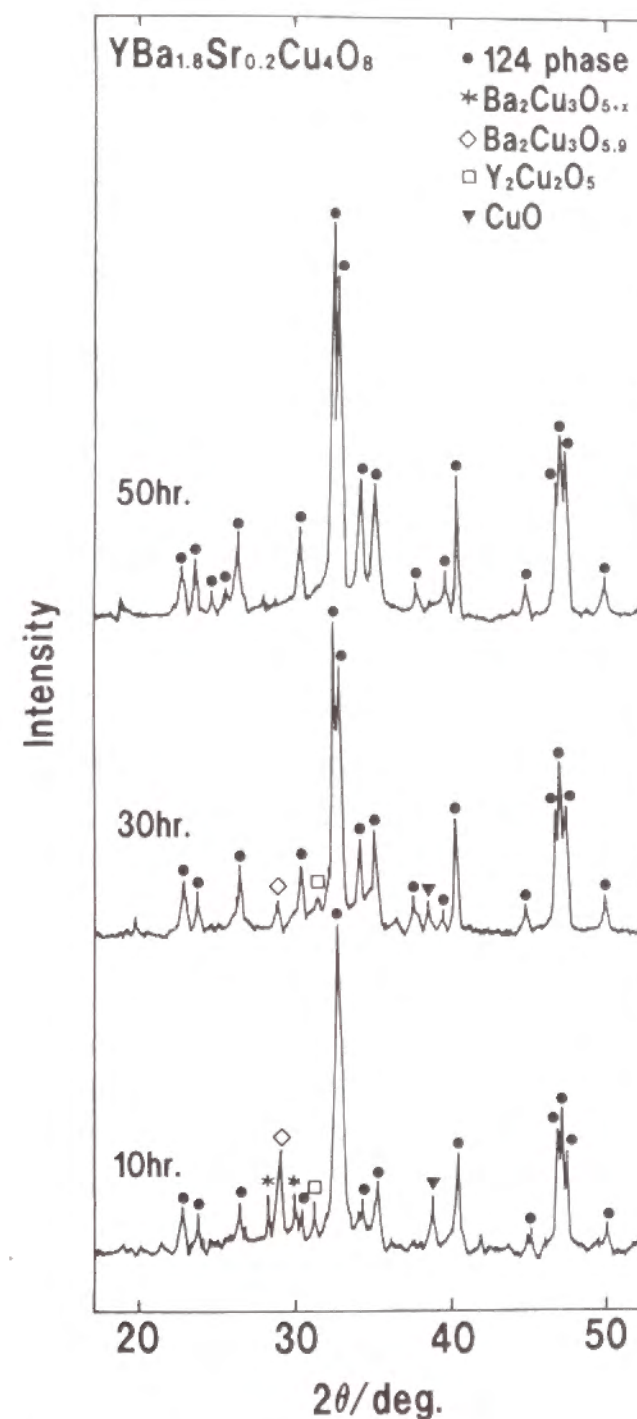


Fig. 3. The XRD patterns of powder products obtained by heating the gel with the composition of $YBa_{1.8}Sr_{0.2}Cu_4O_8$ at 780 °C for 10, 30 and 50 h in flowing oxygen.

Y-124 phase after heating the gel at 780 °C for 10 h. As the heating time increases, the amount of impurity phases decreases and a single phase of $\text{YBa}_{1.8}\text{Sr}_{0.2}\text{Cu}_4\text{O}_8$ is obtained after heating for 50 h.

The XRD patterns of the products of $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_8$ (Y-124(Sr)), $\text{YBa}_{2-x}\text{K}_x\text{Cu}_4\text{O}_{8.5}$ (Y-124(K)) and $\text{YBa}_{2-x}\text{Na}_x\text{Cu}_4\text{O}_{8.5}$ (Y-124(Na)) are shown in Fig. 4, 5 and 6, respectively. These figures indicate that a single phase is obtained for compositions up to $x=0.4$ for Sr, $x=0.2$ for K and $x=0.1$ for Na. For compositions of $x=0.6$ for Sr (Fig. 4), $x=0.3$ for K (Fig. 5) and $x=0.15$ for Na (Fig. 6), impurity phases such as $\text{Y}_2\text{Cu}_2\text{O}_5$, $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$, CuO , Y_2BaCuO_5 or unknown phases remain in the samples after heating for 50 h.

According to the flame spectrometric analysis, only 0.04 wt% loss in the potassium content was observed after the heat-treatment both in $\text{YBa}_{1.9}\text{K}_{0.1}\text{Cu}_4\text{O}_{8.5}$ and $\text{YBa}_{1.8}\text{K}_{0.2}\text{Cu}_4\text{O}_{8.5}$. This confirms that the potassium remains in the sample after the heat-treatment in an amount corresponding to the starting composition.

3.2. Lattice Constants

The lattice constants of the Y-124 phases are shown in Table I and Fig. 7. The values of $\text{YBa}_2\text{Cu}_4\text{O}_8$ are $a=0.3846$ nm, $b=0.3869$ nm and $c=2.723$ nm, which are in good agreement with the values determined with a neutron diffraction method by Lightfoot *et al.* [14]. The lattice constants a , b and c of the Y-124(Sr) phase decrease monotonically with increasing Sr concentration. In the Y-124(K) phase, the lattice constant a slightly decreases with increasing K and the lattice constants b and c remain almost constant. In the Y-124(Na) phase, the lattice constant a decreases with increasing Na, whereas b and c remain constant.

3.3. Oxygen Content

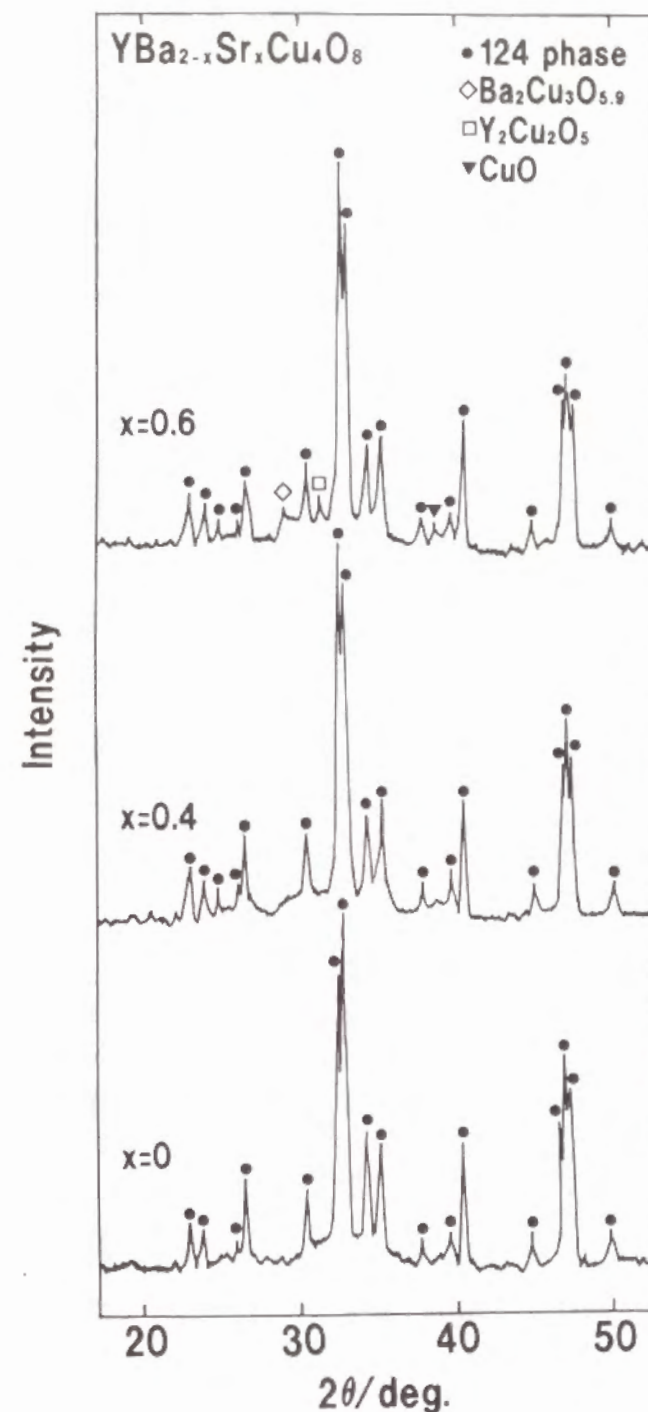


Fig. 4. The XRD patterns of powder products obtained by heating the gel of $\text{YBa}_{2-x}\text{Sr}_x\text{Cu}_4\text{O}_8$ for $x=0$, 0.4 and 0.6 at 780 °C for 30 - 50 h in flowing oxygen.

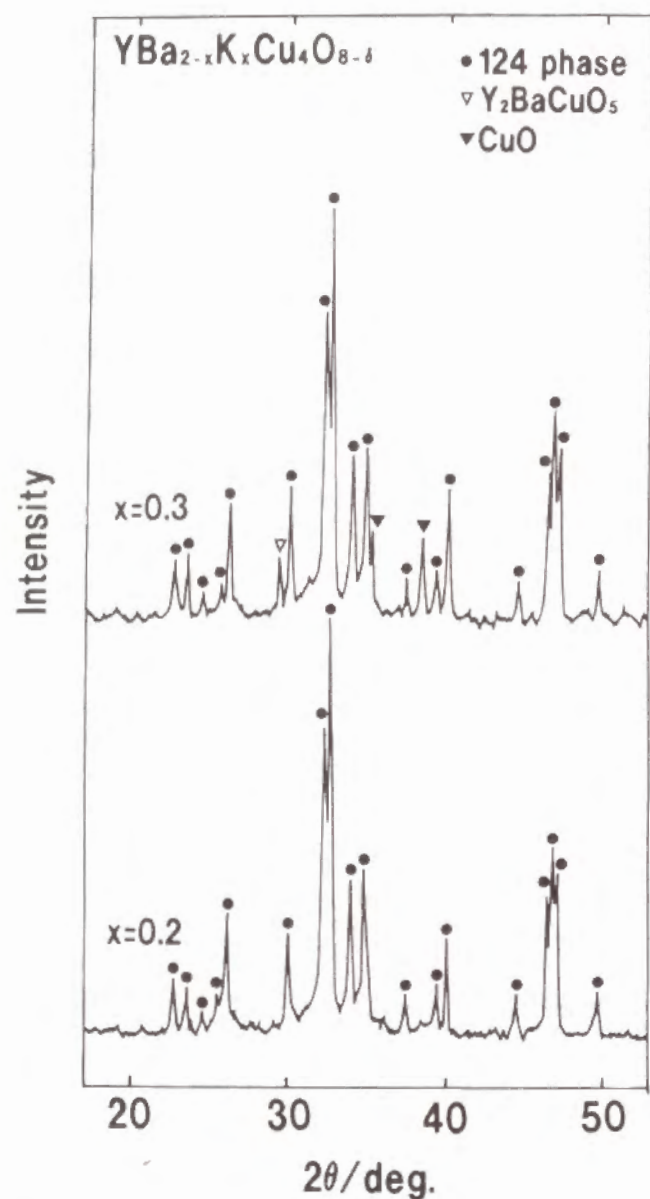


Fig. 5. The XRD patterns of powder products obtained by heating the gel of $\text{YBa}_{2-x}\text{K}_x\text{Cu}_4\text{O}_{8-\delta}$ for $x=0.2$ and 0.3 at 780°C for 30 - 50 h in flowing oxygen.

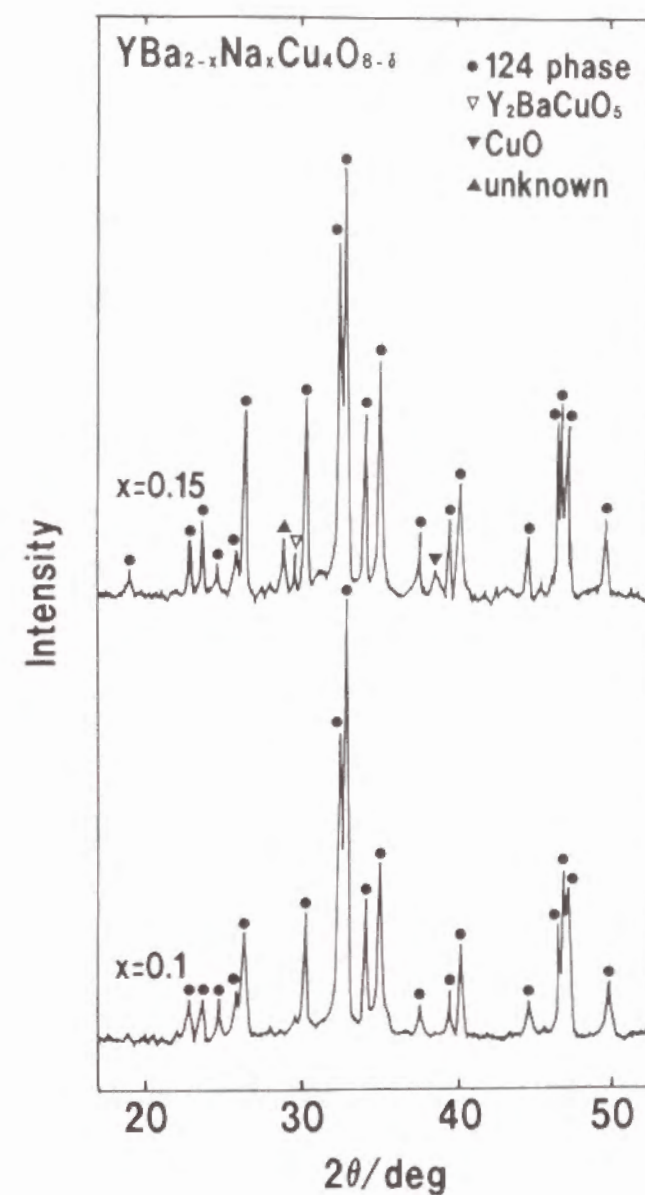


Fig. 6. The XRD patterns of powder products obtained by heating the gel of $\text{YBa}_{2-x}\text{Na}_x\text{Cu}_4\text{O}_{8-\delta}$ for $x=0.1$ and 0.15 at 780°C for 30 - 50 h in flowing oxygen.

Table I The lattice constants and the oxygen content of Ba-site substituted $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_z$ (R=Sr, K or Na).

R_x	Lattice Constants / nm			Oxygen Content
	a	b	c	z
non-substituted	0.3846	0.3869	2.7230	8.04
$\text{Sr}_{0.2}$	0.3837	0.3867	2.7208	7.98
$\text{Sr}_{0.4}$	0.3833	0.3863	2.7154	7.96
* $\text{Sr}_{0.6}$	0.3830	0.3862	2.7144	-
$\text{K}_{0.1}$	0.3843	0.3871	2.7234	7.83
$\text{K}_{0.2}$	0.3842	0.3870	2.7228	7.71
* $\text{K}_{0.3}$	0.3842	0.3871	2.7225	-
$\text{Na}_{0.1}$	0.3843	0.3868	2.7232	7.85
* $\text{Na}_{0.15}$	0.3841	0.3868	2.7225	-
* $\text{Na}_{0.2}$	0.3840	0.3869	2.7222	-

*Not a single phase of the Y-124.

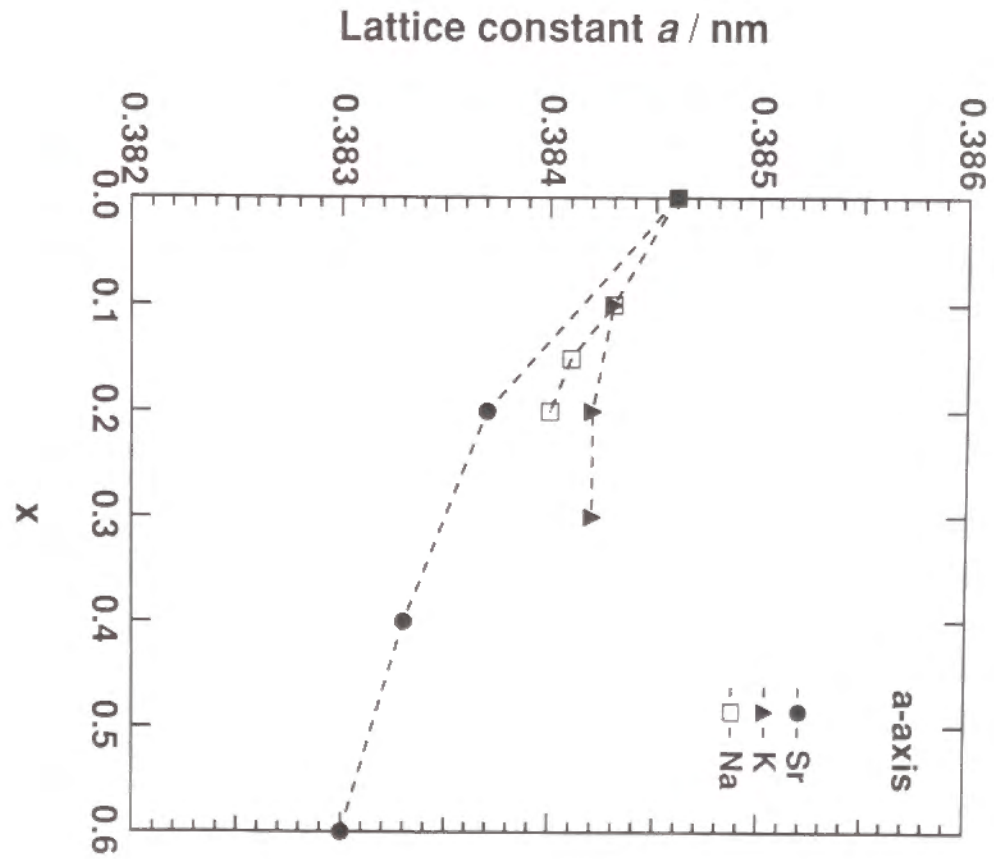


Fig. 7. (a) The lattice constant a of $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$ (R=Sr, K or Na).

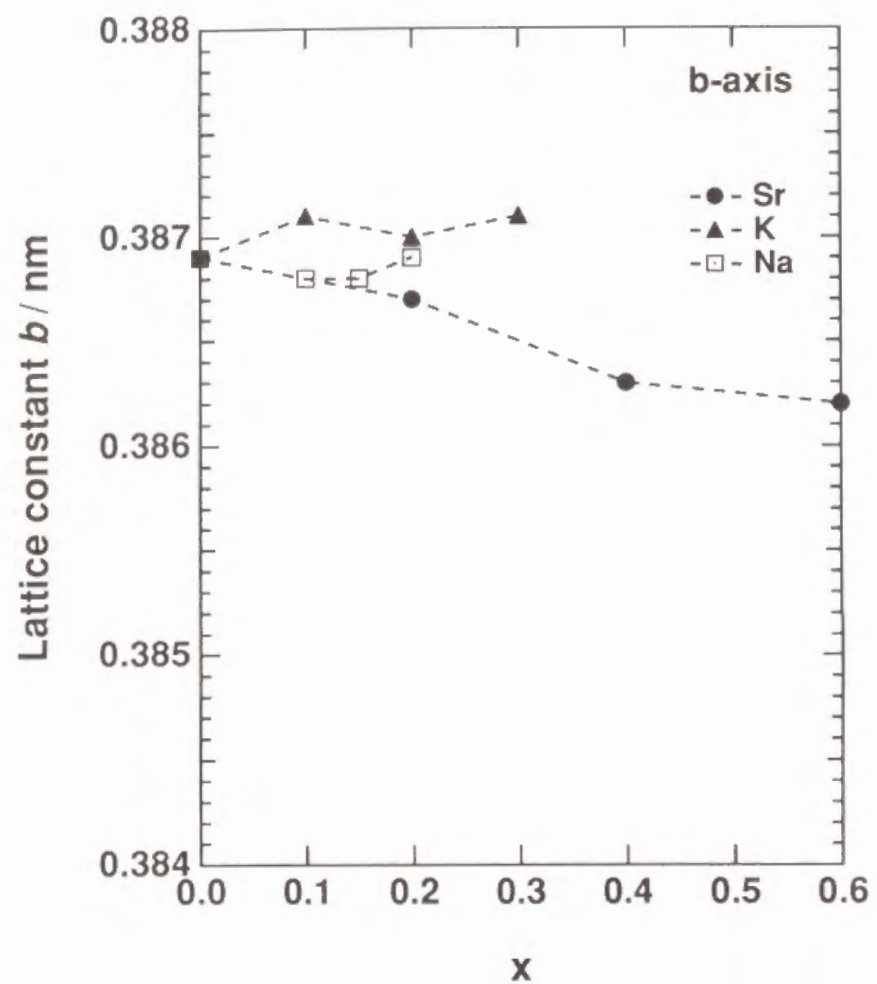


Fig. 7. (b) The lattice constant b of $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$ ($\text{R}=\text{Sr}, \text{K}$ or Na).

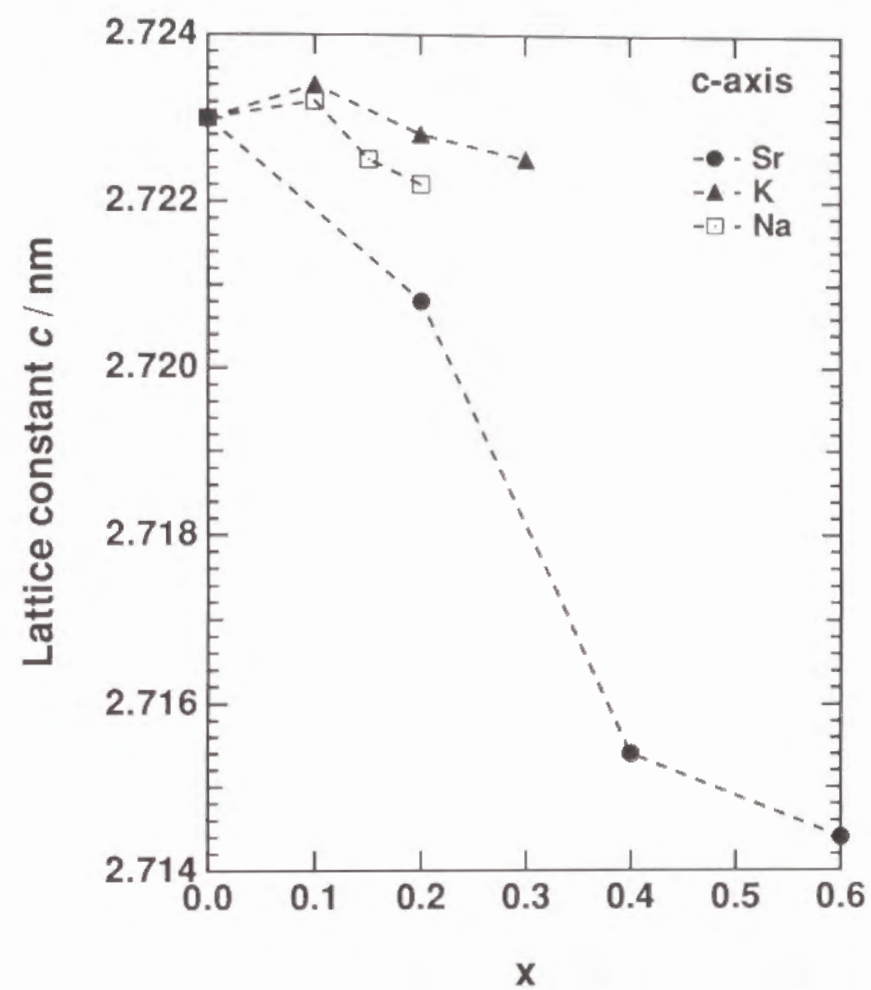


Fig. 7. (c) The lattice constant c of $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$ ($\text{R}=\text{Sr}, \text{K}$ or Na).

The oxygen content of the single-phase products are summarized in Table I. The non-substituted $\text{YBa}_2\text{Cu}_3\text{O}_8$ sample has an oxygen content of 8.04. The Y-124(Sr) samples have oxygen contents of 7.98 for $x=0.2$ and 7.96 for $x=0.4$. All these values are close to a stoichiometric value of 8. On the other hand, the Y-124(K) and Y-124(Na) samples have oxygen contents of 7.83 and 7.71 for $x=0.1$ and 0.2 of K, respectively, and 7.85 for $x=0.1$ of Na, which are appreciably lower than 8. These values are lower than those calculated on the assumption that decrease in charge due to K^+ and Na^+ substitution is compensated by the formation of oxygen vacancies; the calculated values are 7.95 for $x=0.1$ and 7.90 for $x=0.2$.

3.4. Electrical Resistance

The temperature dependence of the electrical resistance of the sintered pellets is shown in Fig. 8. All the samples show superconducting transition and metallic behavior of conduction above T_c . Table II shows T_c (onset) and T_c (end) of the samples. The non-substituted Y-124 sample shows T_c (onset) of 87 K and T_c (end) of 74 K. The Y-124(Sr) phase of $x=0.2$ shows 3 K higher T_c (onset) and 2 K higher T_c (end) than those of the non-substituted Y-124 phase, while the Y-124(Sr) phase of $x=0.4$ shows 2 K lower T_c (end). The Y-124(Sr) phase of $x=0.6$ containing impurity phases shows 3 K lower T_c (end). The Y-124(K) phase of $x=0.1$ and 0.2 shows 1 K lower T_c (onset) and T_c (end), while the Y-124(K) phase of $x=0.3$ with impurity phases shows the same T_c (end) as the non-substituted Y-124 phase. Both the Y-124(Na) phases of $x=0.1$ (single phase) and 0.2 (not single phase) shows 4 K higher T_c (end) than the non-substituted Y-124 phase.

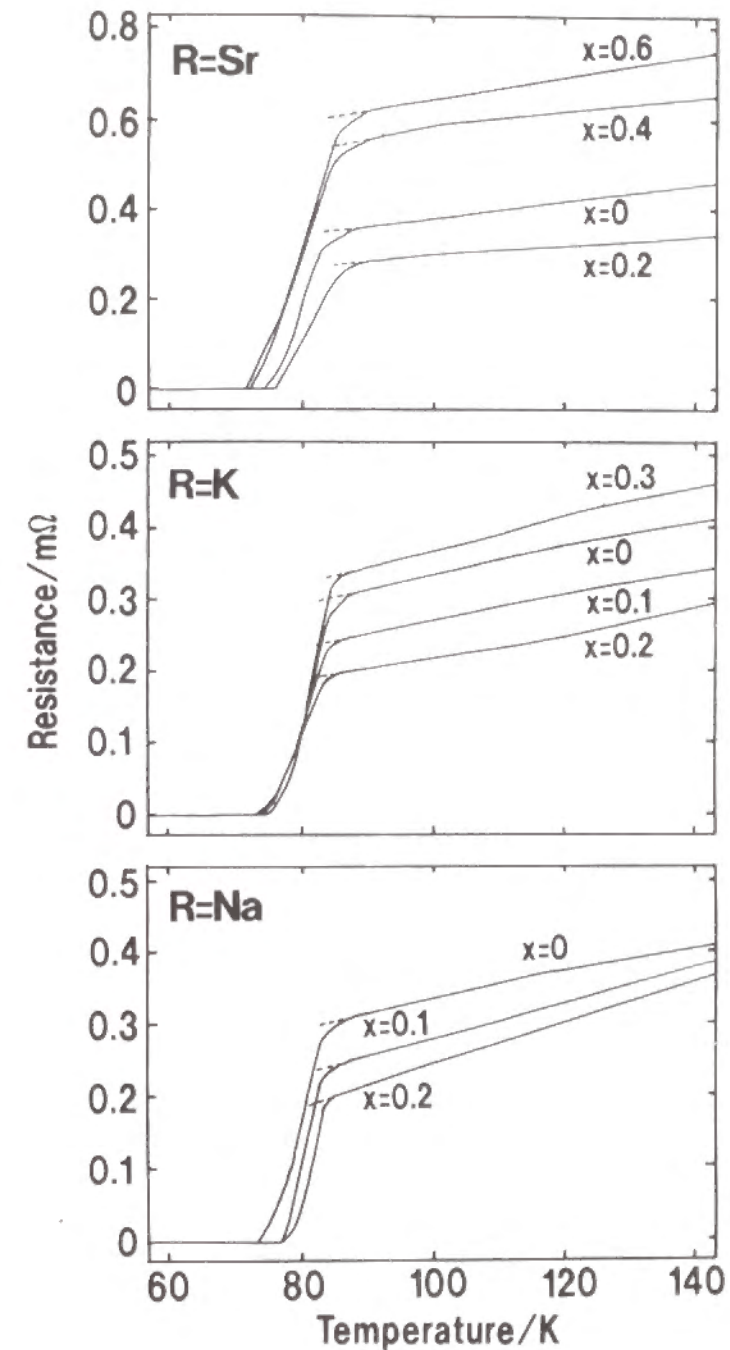


Fig. 8. Temperature dependence of the electrical resistance of $\text{YBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_8$ where R=Sr, K and Na.

Table II The superconducting transition temperature of Ba-site substituted $\text{YBa}_{2-x}\text{R}_x\text{Cu}_3\text{O}_7$ (R=Sr, K or Na).

R_x	$T_c(\text{onset}) / \text{K}$	$T_c(\text{end}) / \text{K}$
non-substituted	87	74
$\text{Sr}_{0.2}$	90	76
$\text{Sr}_{0.4}$	90	72
$\text{K}_{0.1}$	86	73
$\text{K}_{0.2}$	86	73
$\text{Na}_{0.1}$	87	78
* $\text{Na}_{0.2}$	85	78

*Not a single phase of the Y-124.

3.5. SEM Observation

The SEM photographs of sintered pellets of the non-substituted Y-124 phase, Y-124(Sr) phase of $x=0.4$, Y-124(K) phase of $x=0.2$ and Y-124(Na) phase of $x=0.1$ are shown in Fig. 9. It is seen that grains of the Y-124(K) and Y-124(Na) phases are larger than those of the non-substituted Y-124 and Y-124(Sr) phases. The grain sizes are approximately 0.2-1.0 μm for the non-substituted Y-124 and Y-124(Sr) phases, and 1.0 μm for the Y-124(K) and Y-124(Na) phases. It appears that the Y-124(K) and Y-124(Na) pellets, which consist of plate-like grains, are sintered better than the non-substituted Y-124 and Y-124(Sr) pellets, which consist of smaller spherical grains.

4. DISCUSSION

4.1. Changes of Lattice Constants

There are three factors which determine the lattice constants of the present Y-124 phases; (1) ionic radii of Ba^{2+} , Sr^{2+} , K^+ and Na^+ [15], (2) their valence and (3) oxygen vacancies. All the lattice constants a , b and c of the Y-124(Sr) phase decrease with increasing Sr concentration x . In the substitution of Sr for Ba, the valence of cations does not change and accordingly oxygen vacancies are not formed as mentioned in 3.3. Therefore, the changes of the lattice constants are caused by the difference in the ionic radius of Ba^{2+} (0.152 nm) and that of Sr^{2+} (0.136 nm) [15]. Since Sr^{2+} ions are smaller, the introduction of Sr^{2+} ions into Ba-site would contract the lattice. Fig. 7 shows that this is actually the case. It should be noted that a rate of contraction of b -axis with increasing x is smaller than that of a -axis. This may result from the existence of double CuO chains along b -axis as shown in Fig. 1.

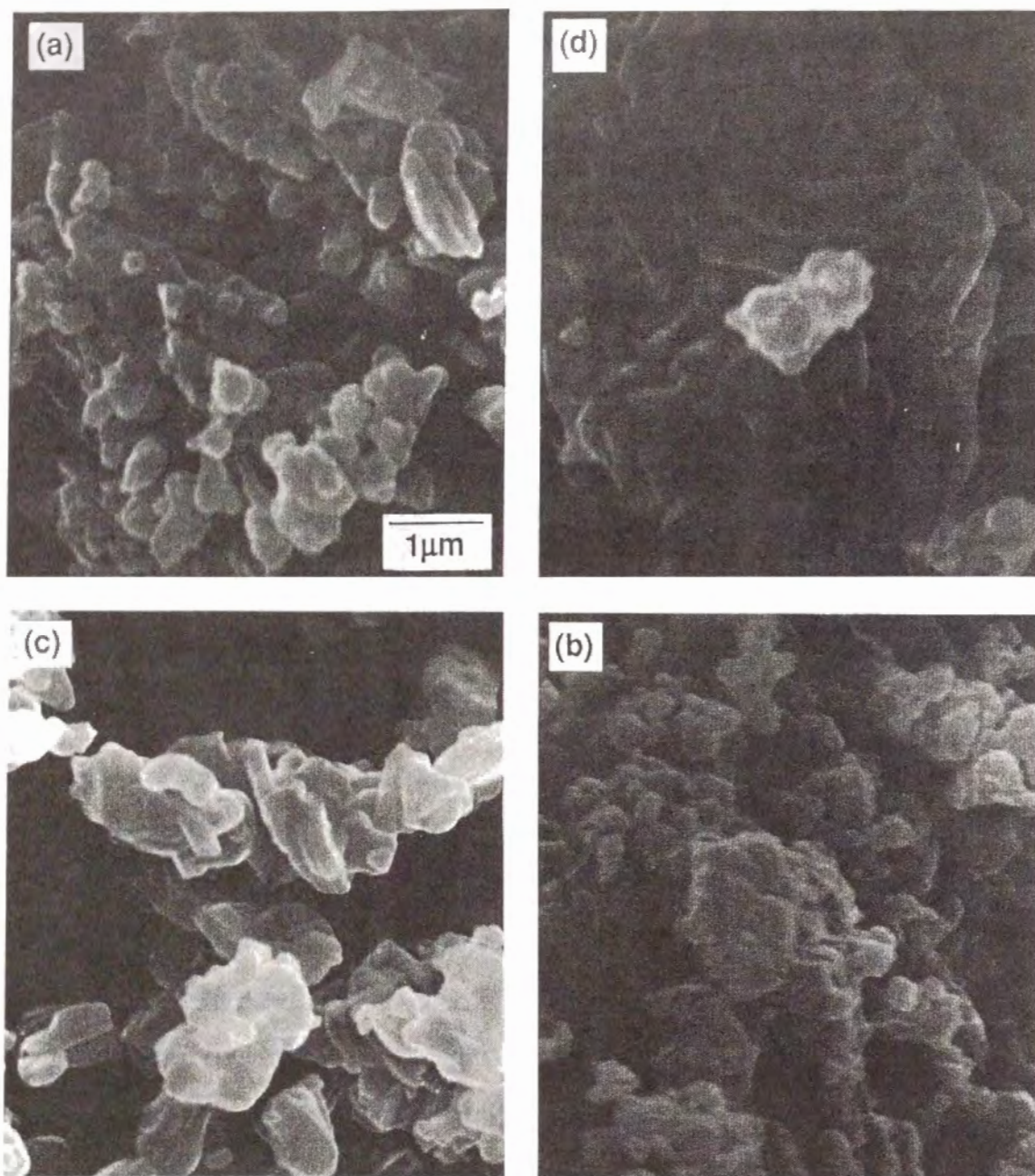


Fig. 9. The SEM photographs of the sintered pellets of $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$; (a) non-substituted Y-124 phase, (b) $\text{R}=\text{Sr}$, $x=0.4$, (c) $\text{R}=\text{Na}$, $x=0.1$ and (d) $\text{R}=\text{K}$, $x=0.2$.

The lattice constant a of the Y-124(K) phase slightly decreases with increasing K concentration, whereas b and c are constant. Since the ionic radii of Ba^{2+} (0.152 nm) and K^+ (0.159 nm) are nearly the same, it is assumed that the difference in valence and the formation of oxygen vacancies affect the lattice constants, which is explained in comparison with the Y-123 phase as follows. In the Y-123 phase, $\text{YBa}_2\text{Cu}_3\text{O}_{7.5}$, the lattice constant a increases and b slightly decreases with increasing oxygen vacancies [16]. As the oxygen content decreases, oxygen vacancies are formed at the O(4) site, *i.e.* in the CuO single chains along b -axis, and, at the same time, occupation of the chain sites along a -axis by oxygen takes place. This may be assumed to correspond to the increase in the lattice constant a and the slight decreases in b with increasing oxygen vacancies in the Y-123 phase. In the Y-124 phase, however, it is thought that oxygen vacancies are less effective on the lattice constants, especially of b and c -axis, than in the Y-123 phase because the number of oxygens at the chain site of the Y-124 phase is twice that of the Y-123 phase. In addition, the effect of one oxygen vacancy formed in one CuO chain in the Y-124 phase may be minimized by the presence of the adjacent CuO chain. These explain the negligible change in the lattice constants b and c in Y-124(K) phase in spite of the changes in the oxygen content.

The slight decrease in a -axis in the Y-124(K) phase may result from the smaller electrostatic interaction between K^+ and the CuO_2 plane. Ba^{2+} ions strongly interact with the CuO_2 plane with a negative charge and shift toward the plane in the direction of c -axis. Because of the smaller positive charge, the interaction of K^+ ions in the Ba-site with the CuO_2 plane may be weaker than Ba^{2+} ions. This would cause a larger $\text{Cu}(2)\text{-O}(2)$ interaction and hence smaller $\text{Cu}(2)\text{-O}(2)$ distance, resulting in contraction of a -axis.

The lattice constant a of the Y-124(Na) phase decreases with increasing Na concentration, which is thought to be caused by the smaller ionic radius of Na^+ (0.124 nm) than that of Ba^{2+} (0.152 nm). The lattice constants b and c of the Y-124(Na) phase remain almost unchanged with increasing Na concentration. It may be possible that the maximum content of Na^+ that forms the single-phase Y-124, $x=0.1$ in the present case, is so low that the change in the lattice constants b and c with the Na concentration might not be clearly detected; the rate of change in the lattice constants b in the Y-124(Sr) phase is, in fact, as small as that in the Y-124(Na) phase in the range of $x = 0 - 0.2$ (see Fig. 7 (b)).

4.2. Effects of Substitution on T_c

We have attempted to change the lattice constants and introduce additional holes by substituting Sr^{2+} , K^+ or Na^+ for Ba^{2+} in $\text{YBa}_2\text{Cu}_4\text{O}_8$. It was observed that the contraction of the lattice, especially those along a - and b -axes for the substitution of Sr^{2+} and Na^+ , increases T_c , although substitution of Sr^{2+} in a large amount of $x = 0.4$ results in a decrease in T_c .

In oxide superconductors in which carriers are holes, a decrease in the bond length of Cu-O in the CuO_2 plane often raises the T_c . Since the high- T_c superconductivity in cuprate superconductors is based upon the hybrid of Cu-3d and O-2p orbitals in the two-dimensionally linked $[\text{CuO}_2]_\infty$ as shown in Fig. 10, the Cu-O bond length would affect the electronic structure and hence T_c . When the Cu-O distance in the plane decreases, the overlap of Cu-3d $_{x^2-y^2}$ and O-2p $_{\sigma}$ orbitals may become larger and the density of carriers may increase. In fact, Liu *et al.* [17] found an increase in T_c with decreasing lattice constants a and b in the rare-earth substituted Y-124 phases.

In contrast to the effect of the lattice constants a and b on T_c , the effect

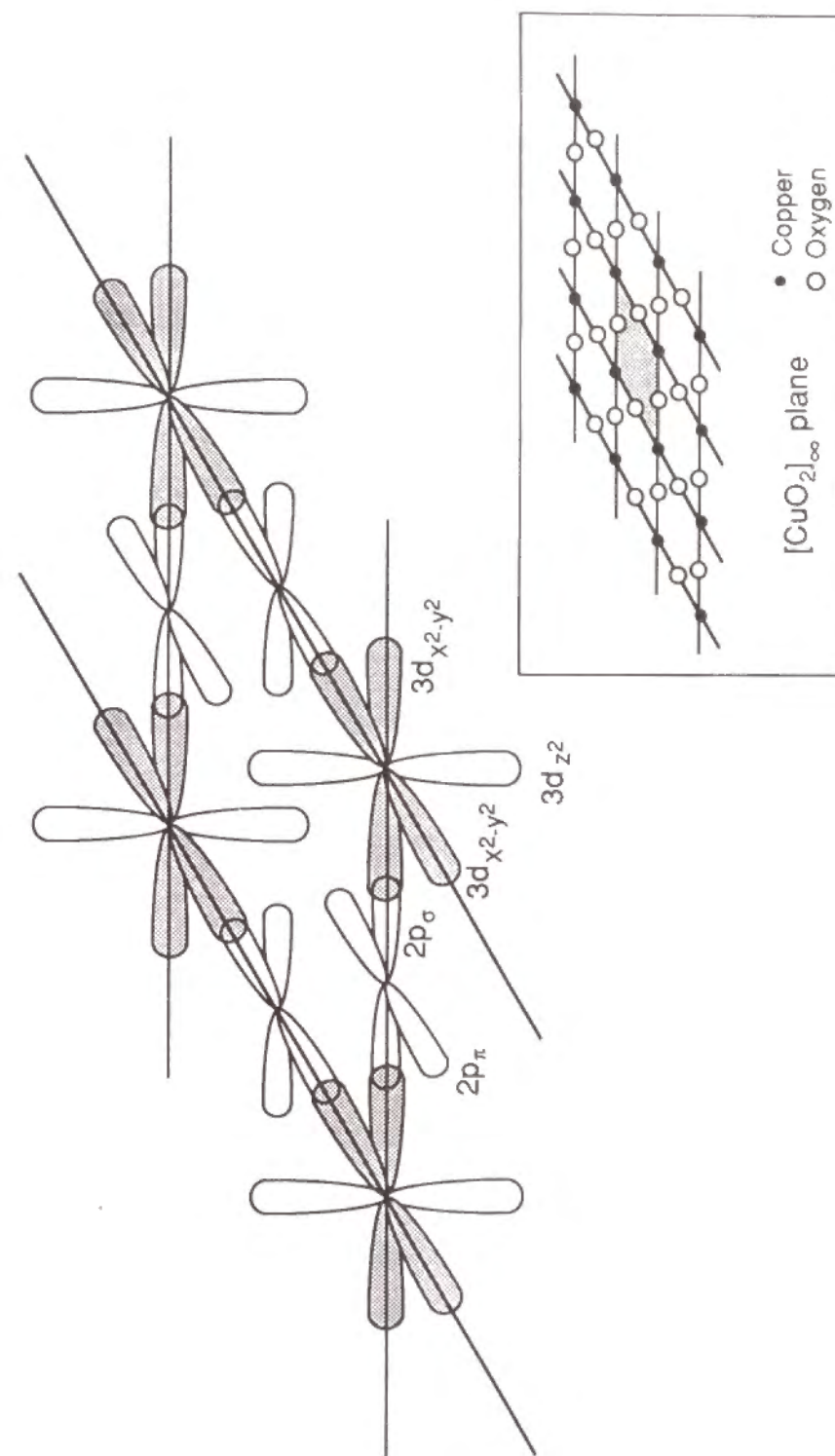


Fig. 10. The overlap of the Cu-3d and O-2p orbitals in the CuO_2 planes.

of the lattice constant c is controversial. In discussing the physical pressure effect, it was shown that T_c of the Y-124 phase increases in proportion to decrease in the lattice constant c because of the redistribution of holes between the CuO chains and the CuO₂ planes, which is caused by the shortening of Cu(2)-O(1) distance [5,18]. Wada *et al.* [19], however, synthesized the Sr-substituted Y-124 phase under high oxygen pressure, reporting that the change in T_c with increasing Sr content or decreasing lattice constant c is negligible. Lately, Ishigaki *et al.* [20] claimed that the distribution of holes in the Sr-substituted Y-124 phase is essentially the same as the non-substituted Y-124 phase at 0 GPa on the basis of the calculation of Madelung energy, taking account of the displacement not only of Cu(2) and O(1) but also of all other ions by Sr substitution.

Although the changes in T_c with the substitution observed in the present study are not quite large, the substitution of smaller cations for Ba²⁺ is likely to increase T_c through decreasing the lattice constants a and b . This was confirmed by substituting three kinds of cations, Sr²⁺, K⁺ and Na⁺, two of which have smaller ionic radii than Ba²⁺ and one has almost the same ionic radius as Ba²⁺. Since the smaller change in the lattice constant c than a was observed, especially in the range of $x = 0 - 0.2$, it can be concluded that the increase in T_c is caused by the contraction of the CuO₂ plane in the present substitution.

The expected increase in T_c (onset) was not observed in the Y-124(K) or Y-124(Na) phases. It is thought that the substitution of alkali cations in the present work is not effective to increase holes in the CuO₂ planes because the oxygen vacancies are formed as a result of the charge compensation. On the other hand, grain growth of the polycrystalline Y-124 phases was promoted by substitution of alkali cations; that is, the grain size increases and the shape of

grains changes from particulate to plate like ones. Therefore, in the Na⁺-substituted sample, YBa_{1.9}Na_{0.1}Cu₄O_{7.85}, the increase in T_c (end) by 4 K may result from the decrease in the weak link of grain boundaries rather than the effect of the lattice contraction.

5. CONCLUSION

The single-phase YBa_{2-x}R_xCu₄O₈ (R=Sr, K, Na) superconductors were successfully prepared by the sol-gel method under ambient pressure, and the effects of the partial substitution of Sr²⁺, K⁺ or Na⁺ for Ba²⁺ on the structure and properties of YBa₂Cu₄O₈ were investigated.

The lattice constants a , b and c of the Y-124 phase monotonically decreased with substitution of Sr for Ba. The slight increase in T_c (onset) and T_c (end) observed at $x=0.2$ was attributed to the lattice contraction in the CuO₂ plane.

The lattice constant a of the Y-124 phase slightly decreased and b and c did not change with substitution of K. The oxygen content decreased and T_c hardly changed with substitution of K. An expected increase in T_c by hole-doping could not be achieved because the charge compensation was not made by the formation of holes but by the formation of oxygen vacancies.

The lattice constant a of the Y-124 phase decreased and b and c did not change with substitution of Na for Ba. The oxygen content decreased and T_c (onset) hardly changed with substitution of Na as in the case of that of K. T_c (end), however, rose by 4 K on substitution of Na for Ba, probably due to the lattice contraction in the CuO₂ plane and/or the decrease in the weak link of grain boundaries.

Grain growth and change in the shape of the grains from particulate to plate-like ones were observed in the K- and Na-substituted Y-124 samples.

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SECTION 2 EFFECTS OF SUBSTITUTION OF Li FOR Cu ON THE SUPERCONDUCTIVITY OF $\text{YBa}_2\text{Cu}_4\text{O}_8$

1. INTRODUCTION

In order to investigate the mechanism of high-temperature superconductivity in copper oxide superconductors, it is of fundamental significance to examine the effects of the replacement of copper by other elements, because such substitution directly affects the electronic and magnetic structure of the CuO_2 planes which are responsible for electrical conduction. According to the studies previously reported [1,2], the substitution at Cu-sites drastically lowers superconducting transition temperature T_c regardless of the kind of substituting elements, even if the amount of substituents are very small. The destruction of superconductivity is attributed to the magnetic moment arising from the substitution [3]. Therefore, it is thought that the substituents in Cu-site act as magnetic impurities.

Among the substituents at Cu-site, however, lithium shows some interesting effects. Kawai *et al.* [4] reported that T_c of the Bi-2212 phase increases by addition of lithium, which is considered to be substituted for copper. This result attracted much attention as the unique case in which Cu-site substitution can raise T_c . The reason for the increase in T_c , however, has not been clearly explained because of the complexity of the Bi-Sr-Ca-Cu-O system; *i.e.* the Bi-system has three superconducting phases, the Bi-2223, Bi-2212 and Bi-2201 with T_c of 110 K, 80 K and 8 K, respectively, and none of them can be easily obtained as a pure single phase. In addition, there are two cations (Bi

and Cu) with variable valences. Consequently, some reasons for the increase in T_c by lithium addition have been suggested to be due to such as change of cation ratio, presence of a small amount of Bi-2223 phase or change of carrier concentration.

In $\text{YBa}_2\text{Cu}_3\text{O}_y$ (Y-123), which can be easily produced as a single phase and has only one ion, copper, with variable valences, Feduzi *et al.* [5] reported that the lithium substitution for Cu causes a decrease in T_c . However, because the decrease in T_c is considered to result from a decrease in the hole concentration due to the oxygen loss by the charge compensation, an actual role of lithium itself at Cu-site cannot be understood.

On the contrary, since $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124), which is distinguished from $\text{YBa}_2\text{Cu}_3\text{O}_y$ in the number of CuO chains in the structure, has more thermally stable oxygen content up to 850°C than $\text{YBa}_2\text{Cu}_3\text{O}_y$ [6], the role of lithium as a substituent in the Y-124 phase is thought to become much clearer than in the Y-123. In addition, the substitution of Li^+ for Cu^{2+} may change both hole concentration and T_c , as observed in the substitution of Ca^{2+} for Y^{3+} in the Y-124 which changes the hole concentration and raises T_c from 80 K to 90 K [7]. In this section, effects of the lithium substitution for copper on the superconductivity of $\text{YBa}_2\text{Cu}_4\text{O}_8$ have been examined in order to clarify the role of lithium as a dopant to copper oxide superconductors. $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ was prepared by the sol-gel method [8] and the subsequent heat-treatment under 1 atm oxygen, and the lattice constants, oxygen content, electrical resistance and magnetic susceptibility were measured.

2. EXPERIMENTAL

2.1. Sample Preparation

Samples were prepared by the sol-gel method using metal acetates as starting materials after the experimental procedure described in Chapter 1. $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, $\text{Ba}(\text{CH}_3\text{COO})_2$, $\text{Cu}(\text{CH}_3\text{COO})_2$ and $\text{CH}_3\text{COOLi} \cdot \text{H}_2\text{O}$ (Wako Pure Chemicals, Osaka, Japan) were dissolved in distilled water to make an aqueous solution with a cation molar ratio of $\text{Y}:\text{Ba}:\text{Cu}:\text{Li}=1:2:(4-x):x$ ($x=0, 0.03, 0.05, 0.08, 0.10$ and 0.20). After stirring for 1 h, an aqueous solution of tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$) was added to the acetate solution. The resultant solution was stirred for another 2 h and concentrated in an oven at 80°C . After two days a dried gel with blue color was obtained. The gel was pulverized, heated to 780°C at a rate of 160°C/h in flowing oxygen of 1 atm, kept at 780°C for 2 h and cooled in the furnace. The resultant powder with black color was pressed into pellets with 13 mm diameter and about 1 mm thick under a pressure of 60 MPa and heated at 780°C for 30-50 h with intermittent grinding and pelletizing. For comparison, the Li-free and Cu-deficient sample of the nominal $\text{YBa}_2\text{Cu}_{3.92}\text{O}_8$ was prepared by the same process as described above.

2.2. X-Ray Analysis

The crystalline phases evolved in the samples were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the Y-124 phases were determined by the internal standard method using Si.

2.3. Iodometric Titration

The oxygen content of some samples were determined by the iodometric titration technique, which was described minutely in 2.3, Section 1, Chapter

2.

2.4. Measurement of Superconductivity

The d.c. electrical resistance of the samples was measured by a four probe method and the a.c. magnetic susceptibility of the samples was measured by a Hartshorn bridge method, at temperatures from 300 to 50 K with a Chino Instrument Company superconductivity test system.

3. RESULTS

3.1. Formation of the Y-124 Phases

Figure 1 shows the XRD patterns of the $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ samples with varying x from 0 to 0.20. The Li-free Y-124 phase was obtained as a single phase by heating at 780°C for 30h in flowing oxygen. The Li-substituted Y-124 samples with $x=0.03, 0.05$ and 0.08 was also obtained as a single phase by the same heat-treatment as that for the Li-free Y-124 sample. On the other hand, impurity phases remained in the sample and a single phase of the Y-124 was not obtained for $x=0.10$ and 0.20 , even when the heating time was prolonged up to 50 h. Oxygen contents of both the pure Y-124 and Li-substituted Y-124 of $x=0.08$ were determined to be 8.0 by the iodometric titration.

Figure 2 shows the XRD pattern of the Li-free $\text{YBa}_2\text{Cu}_{3.92}\text{O}_8$ sample heated at 780°C for 30 h in O_2 . It is seen that the Y-124 phase is not formed and, instead, Y-123, BaCuO_2 and CuO are formed.

3.2. Lattice Constants

The lattice constants a , b and c of the Li-substituted Y-124 phases are

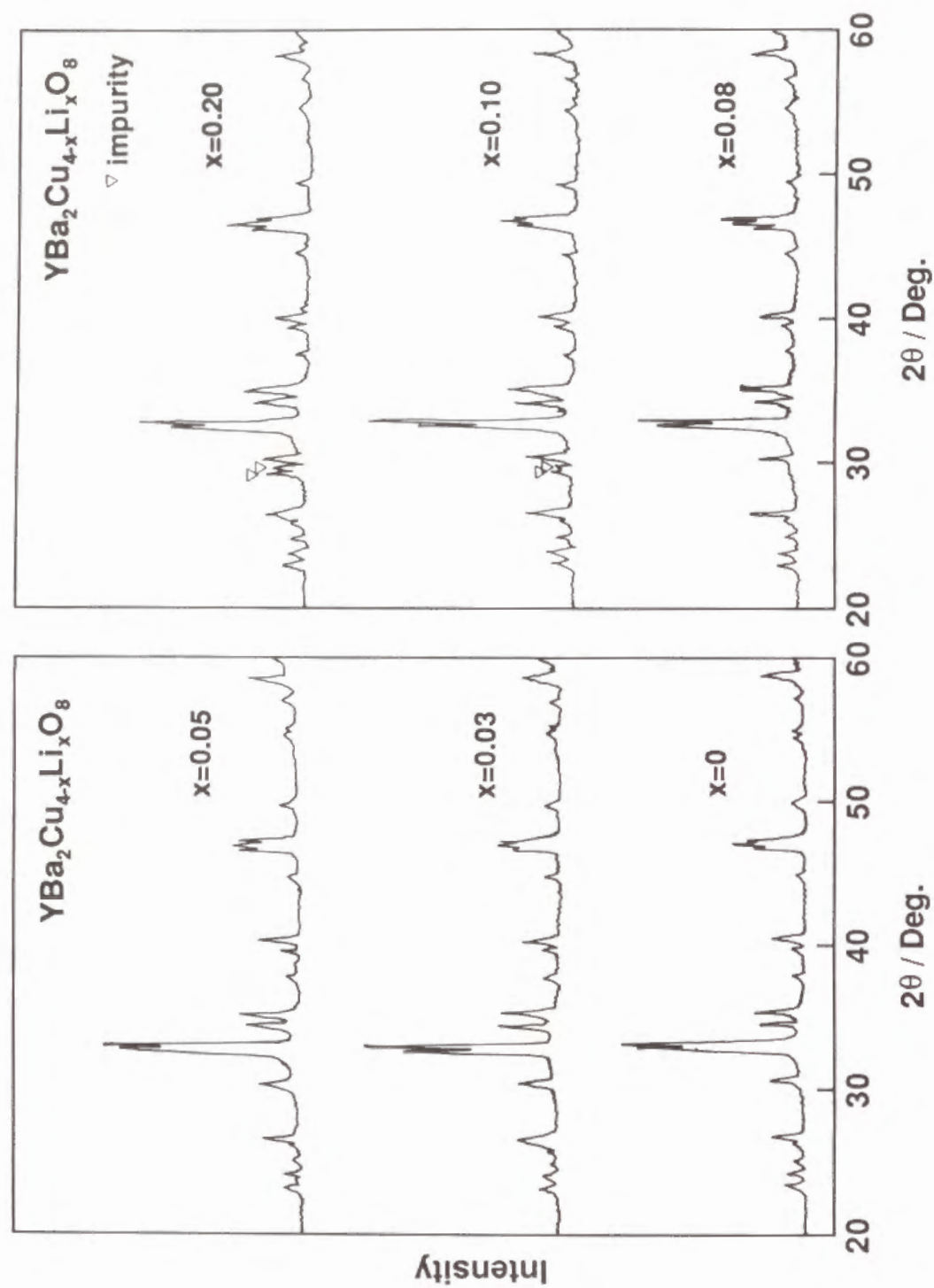


Fig. 1. The XRD patterns of the $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ samples in the range $0 \leq x \leq 0.20$ after the heat-treatment at 780°C for 30 h in O_2 .

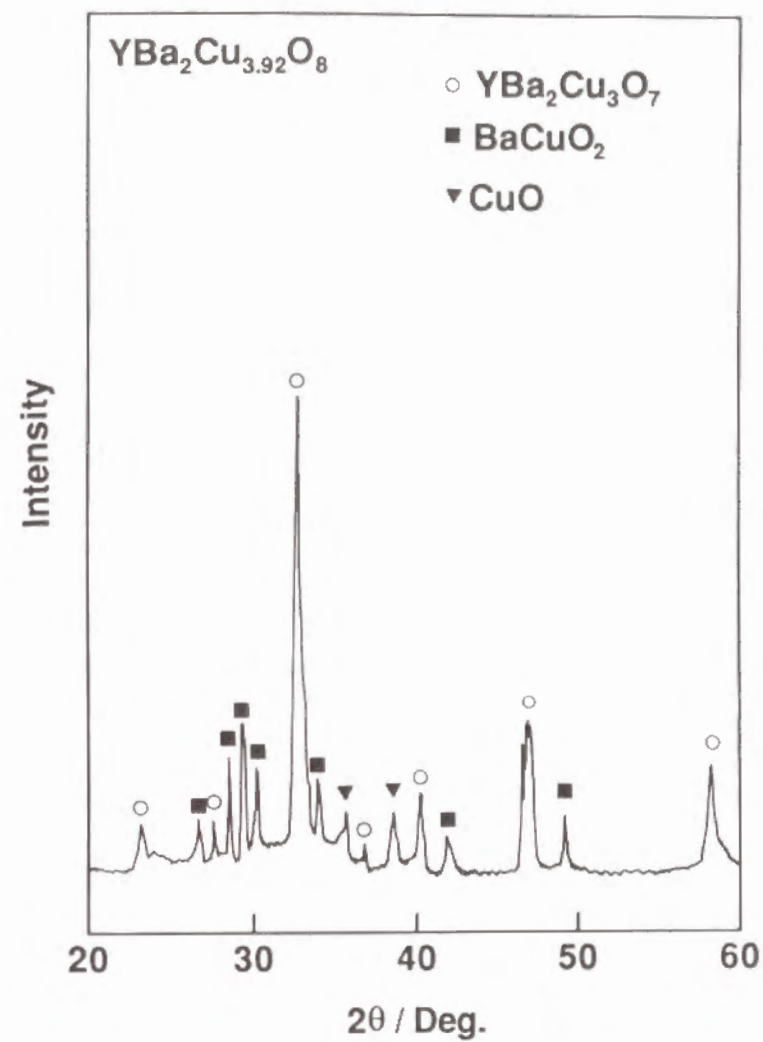


Fig. 2. The XRD patterns of the sample of the nominal composition of $\text{YBa}_2\text{Cu}_{3.92}\text{O}_8$ obtained by heating at 780°C for 30 h in O_2 .

summarized in Table I and shown in Fig. 3. The values for the Li-free Y-124 are $a=0.3846$, $b=0.3869$ and $c=2.721$ nm, which are in good agreement with those reported previously [9,10]. It is seen from Fig. 3 that all the lattice constants a , b and c are almost constant with increasing Li content x within the experimental error.

3.3. Electrical Resistance and Magnetic Susceptibility

The temperature dependence of the electrical resistance of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ with $x=0, 0.03, 0.05$ and 0.08 are shown in Fig. 4. All the samples show metallic conductivity with decreasing temperature and superconducting transition at 75-83 K. Figure 5 shows T_c (onset) and T_c (end) plotted against Li content x , and the values of T_c are summarized in Table II. T_c (onset) decreases monotonically with increasing x up to 0.05, remains constant from $x=0.05$ to 0.10 and decreases again at $x=0.20$. T_c (end) decreases similarly with increasing x up to 0.05 and then keeps a constant value of 66 K from $x=0.05$ to 0.20. Note that the samples of $x=0.10$ and 0.20 are not the single phase of Y-124.

Figure 6 shows the temperature dependence of the a.c. magnetic susceptibility of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$. It is seen that diamagnetism appears in all the samples at temperatures 2-6 K lower than T_c (end) observed in electrical resistance. Superconducting transition temperature $T_c(\chi)$, which was determined from the susceptibility curve, are plotted against Li content x in Fig. 5 and summarized in Table II. $T_c(\chi)$ decreases in a similar manner to T_c (onset) as the Li content x increases from $x=0$ to 0.20.

4. DISCUSSION

Table I The lattice constants of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$.

Lithium Content x	Lattice Constants / nm		
	a	b	c
0	0.3846	0.3869	2.721
0.03	0.3844	0.3867	2.722
0.05	0.3848	0.3868	2.721
0.08	0.3846	0.3868	2.723
*0.10	0.3844	0.3868	2.724
*0.20	0.3847	0.3868	2.723

*Not a single phase of the 124.

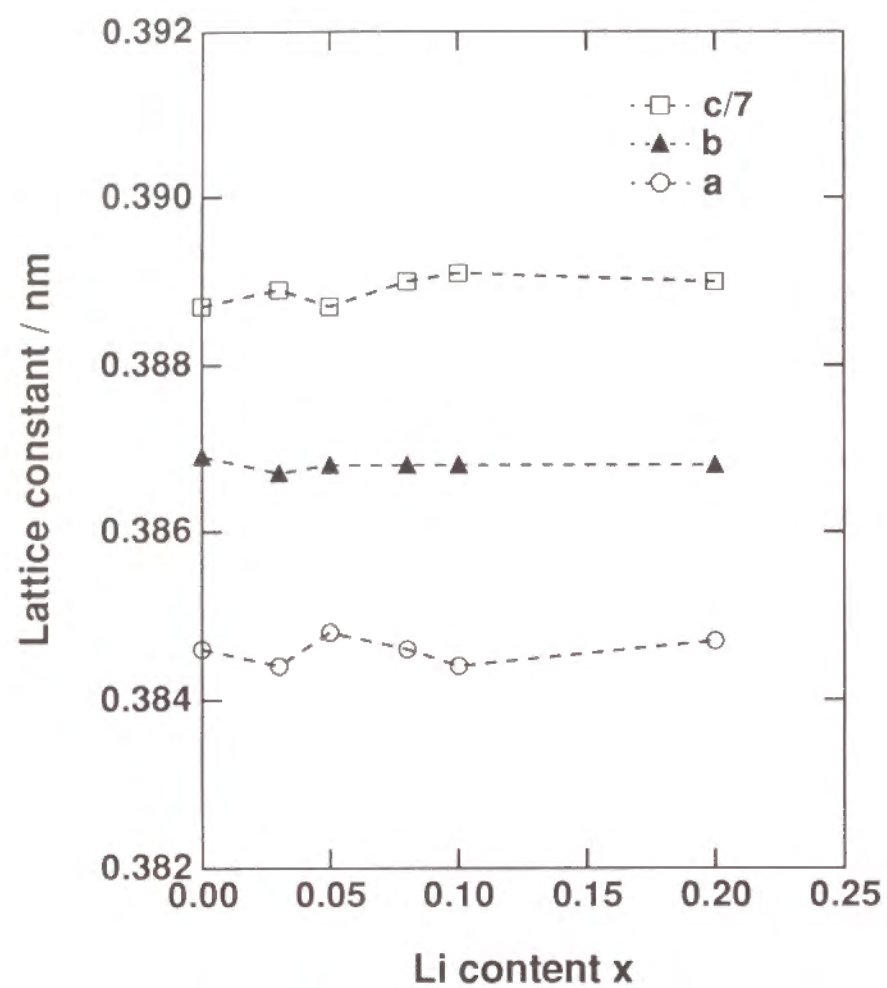


Fig. 3. The lattice constants a , b and c of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ as a function of x .

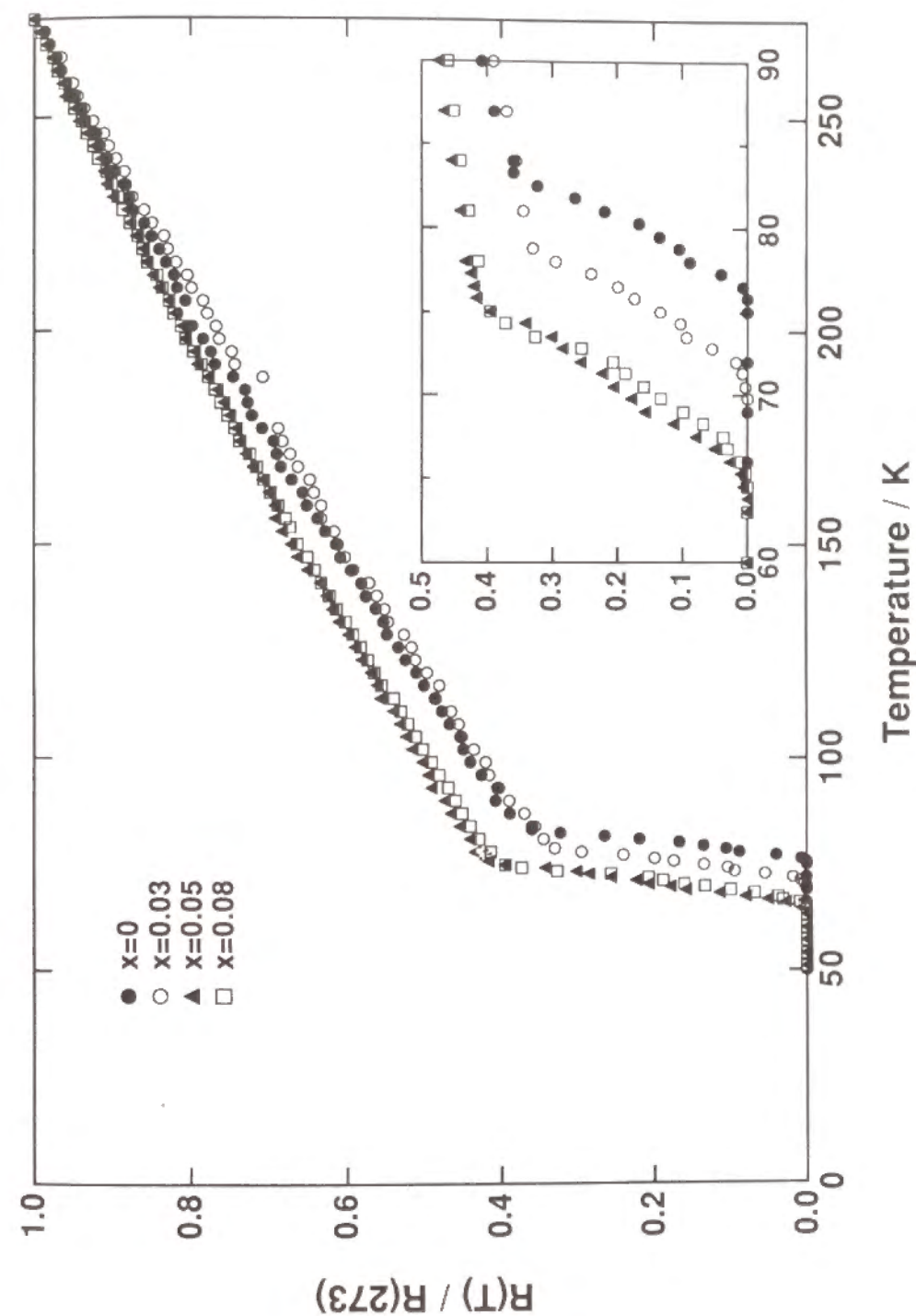


Fig. 4. The temperature dependence of the normalized resistance of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$.

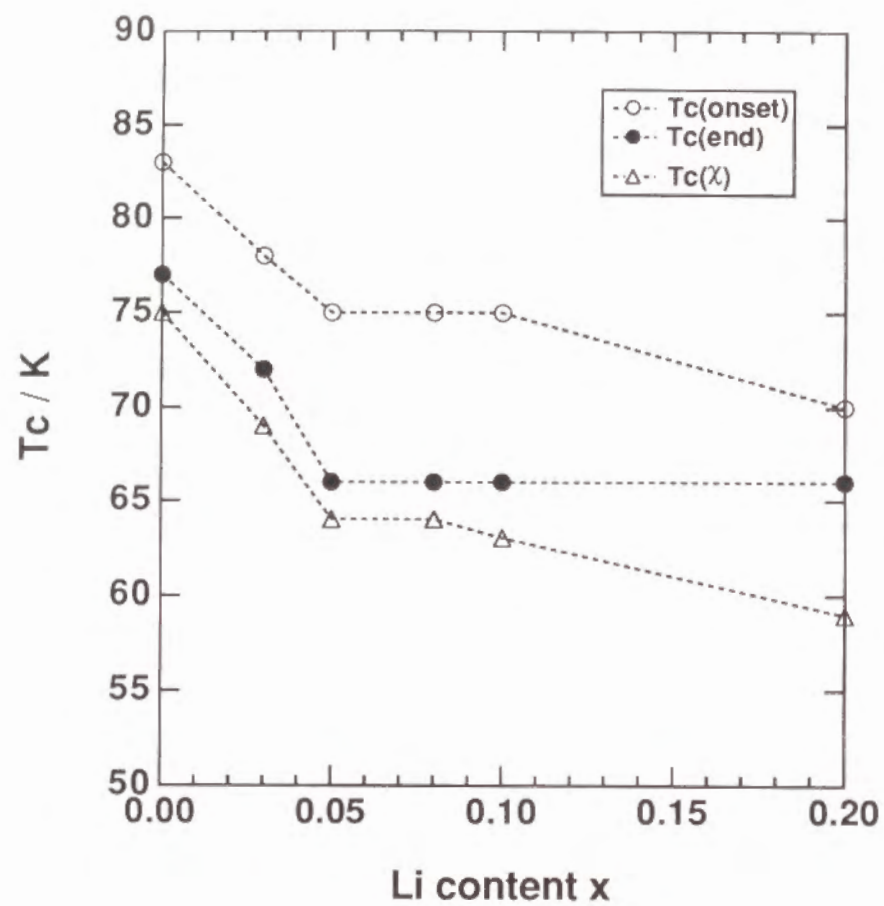


Fig. 5. The superconducting transition temperature of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ as a function of x .

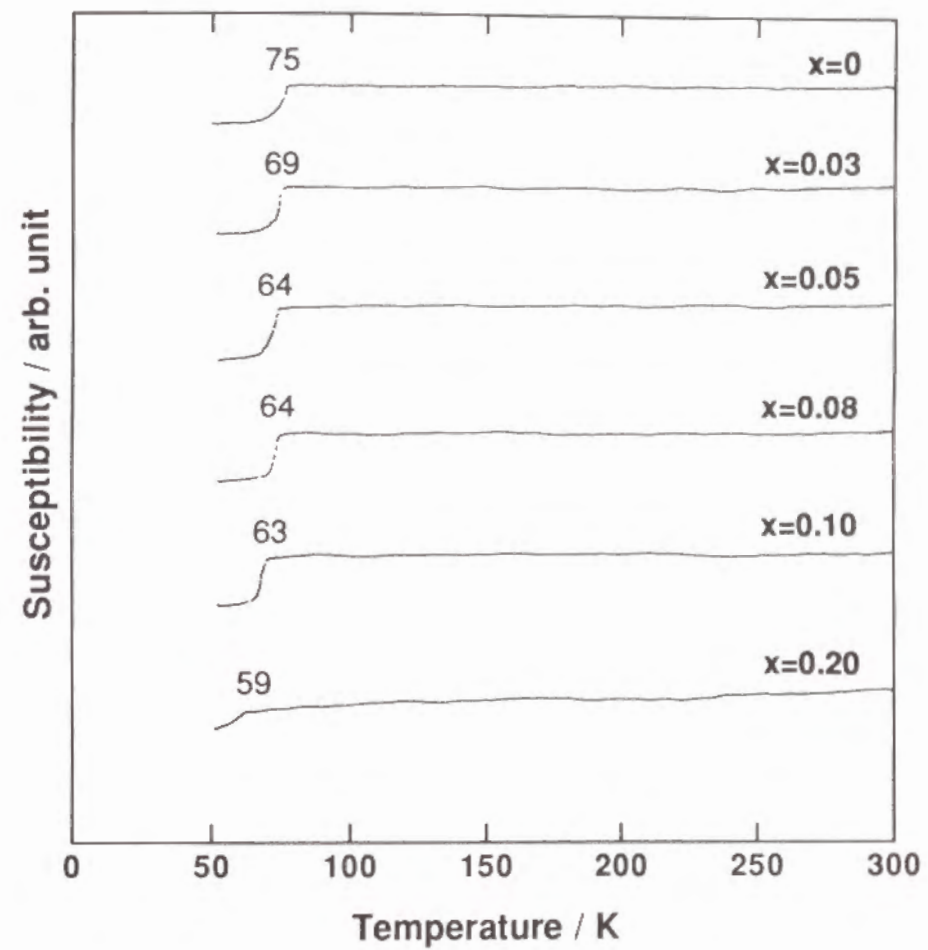


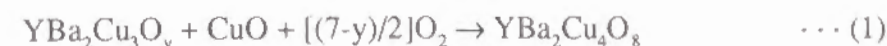
Fig. 6. The temperature dependence of the a.c. magnetic susceptibility of the $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ samples.

Table II Superconducting transition temperature of $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$

x	T_c (onset) /K	T_c (end) /K	T_c (χ) /K
0	83	77	75
0.03	78	72	69
0.05	75	66	64
0.08	75	66	64
0.10	75	66	63
0.20	70	66	59

4.1. Effects of Li Substitution on the Formation and Structure of $\text{YBa}_2\text{Cu}_4\text{O}_8$

As seen from Fig. 2, the Cu-deficient composition of $\text{YBa}_2\text{Cu}_{3.92}\text{O}_y$ does not form the Y-124 phase. This is probably due to the retarded formation reaction of the Y-124. As mentioned in Section 2, Chapter 1, the Y-124 phase is formed from the gel via the following two reactions that proceed simultaneously;



It should be noted, however, that in the $\text{YBa}_2\text{Cu}_{3.92}\text{O}_y$ gel a large amount of BaCuO_2 is precipitated in addition to $\text{YBa}_2\text{Cu}_3\text{O}_y$ and CuO when heated for 30 h, and no $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$, which is an important intermediate for the Y-124 formation, is found. These indicate that, first, the reaction (2) does not take place and, second, the rate of reaction (1) is much lowered because a large amount of BaCuO_2 grains prevent the direct contact of the $\text{YBa}_2\text{Cu}_3\text{O}_y$ and CuO grains not to form the Y-124 phase. On the contrary, the composition of $\text{YBa}_2\text{Cu}_{3.92}\text{Li}_{0.08}\text{O}_8$, corresponding to $\text{YBa}_2\text{Cu}_{3.92}\text{O}_y$ where the Cu defect sites are filled with Li, could form the single-phase Y-124 as shown in Fig. 1. It is considered, therefore, that Li can work as the substituent for Cu, leading to the formation of the Y-124 phase in the $\text{YBa}_2\text{Cu}_{3.92}\text{Li}_{0.08}\text{O}_8$ composition.

According to the report by Feduzi *et al.* [5], 10 % of Cu can be replaced by Li in the $\text{YBa}_2\text{Cu}_3\text{O}_y$ samples through the solid-state reaction. On the other hand, in the present $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ samples the solubility limit of Li is around $x=0.08$, which corresponds to 2 % of Cu. Therefore, it is likely that Li can more easily be substituted for Cu in the Y-123 phase than in the Y-124 phase.

The difference in the solubility of Li between the Y-123 and the Y-124 phases may arise from the difference in the formation process between them as well as the structural difference; that is, the Y-124 has more complicated formation process than the Y-123 as mentioned above.

$\text{YBa}_2\text{Cu}_4\text{O}_8$ has two different Cu-sites that can be occupied by lithium, namely, Cu(1) of the double CuO chains and Cu(2) of the CuO_2 planes. According to Felner *et al.* [11], Fe ions occupy preferentially the Cu(1) sites while Zn ions prefer the Cu(2) sites, and it is likely that the valence of the substituent ions determines the Cu-sites to be occupied. That is, ions with valences higher than +2 tend to occupy Cu(1) site while those with +2 or +1 tend to occupy Cu(2) site. Therefore, it is probable that Li^+ ions are substituted for the Cu(2) site in the present samples. It should be mentioned that in the Y-123 Li^+ ions occupy the Cu(2) sites located in the CuO_2 planes, as reported by Feduzi *et al* [5].

As seen in Fig. 3, the lattice constants are almost constant with changing x in $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$, which may result from the similar ionic radius between Cu^{2+} (0.73 nm) and Li^+ (0.76 nm) [12]. Feduzi *et al.* [5] reported that the lattice constant c slightly decreases with increasing Li content in the Y-123. In the present Y-124, however, it is difficult to observe the change in the lattice constant c by the Li substitution because of the lower solubility of Li, which is one fifth of that in the Y-123.

4.2. Changes in Superconducting Properties by the Li Substitution

The formal charge of Cu in the $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ sample with $x=0.08$ was determined to be +2.27(6) by iodometric titration, which is higher than that in $\text{YBa}_2\text{Cu}_4\text{O}_8$, +2.25. This increase in the formal Cu charge is comparable to that in the Ca-substituted $\text{Y}_{0.9}\text{Ca}_{0.1}\text{Ba}_2\text{Cu}_4\text{O}_8$, +2.275, indicating that additional

holes could be introduced in the present sample. However, in contrast to the fact that Ca substitution can raise the T_c of the 124 from 80 to 90 K [7], the present Li-substituted samples exhibited the decrease in T_c with increasing Li content x as shown in Fig. 5. It is considered, therefore, that the substitution of the Cu-site is crucial to the superconductivity even in the case of Li; that is, the substituents for Cu always diminish T_c or destroy superconductivity of the copper oxide systems.

Xiao *et al.* [3] reported that the Cu-site substitution in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ reduced T_c regardless of the magnetic or non-magnetic substituents and interpreted this as a result of the emerging magnetism in the CuO_2 planes arising from $S=1/2$ spin of Cu^{2+} , which leads to the magnetic pair-breaking effect. Felner *et al.* [11] reported that in the Y-124 both magnetic Fe ions in the Cu(1) and non-magnetic Zn ions in the Cu(2) largely suppress superconductivity. Since Li ions are not magnetic, the decrease in T_c in the present samples is probably attributed to the magnetic moment in the CuO_2 planes emerging on the Li-substitution for the Cu(2) ions. If Li^+ ions did not occupy the Cu(2) site, T_c might increase because of the introduced holes.

The decreasing rate of T_c , dT_c/dx , in the present $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ is about -1.4×10^2 K, which is somewhat smaller than that in $\text{YBa}_2\text{Cu}_{4-x}\text{M}_x\text{O}_8$ ($M=\text{Fe}, \text{Zn}$) [11], $dT_c/dx \approx -6.9 \times 10^2$ K. This may result from the effects of the different valent substituents occupying the Cu-site. Malik *et al.* [13] reported that the substitution of Ag for Cu in $\text{La}_{1.8}\text{Sr}_{0.2}\text{Cu}_{1-x}\text{Ag}_x\text{O}_{4.6}$ depressed T_c by 50 % at $x=0.15$, which is much less than the effect of the other substituents [3] such as Fe, Co, Ni, Zn, etc. Since Ag is ordinarily a monovalent ion as Li in the present case, it is likely that the substitution of monovalent ions for Cu is less effective to suppress the superconductivity than multivalent ion, which is thought

to result from the effect of the introduced holes by the substitution. The holes may prevent the appearance of the Cu^{2+} spin.

5. CONCLUSION

The single-phase superconducting $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$ was successfully prepared by the sol-gel method, and the effects of the Li substitution on the formation, structure and superconducting properties were examined. A single phase of the Y-124 was obtained in the range $0 \leq x \leq 0.08$, while impurity phases appeared over $x=0.10$. The lattice constants were almost constant with increasing x , probably due to the similar ionic radius between Cu^{2+} and Li^+ . The superconducting transition temperature decreased monotonically with increasing lithium content. The suppression of superconductivity by the Li substitution was attributed to the impurity effect in the CuO_2 planes, which gives rise to the magnetic moment.

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CHAPTER 3

STRUCTURE AND PROPERTIES OF NdNiO_{3-y} PREPARED BY THE SOL-GEL METHOD

1. INTRODUCTION

The discovery of high temperature superconductivity in copper oxide systems [1-3] has aroused renewed attention to 3d transition metal oxide systems. In particular, the perovskite-related rare earth transition metal oxides with metallic conductivity are of great interest in understanding the mechanism of superconductivity and searching for new superconducting materials. Perovskite-type RNiO_3 's (R=rare earth element) show some different behavior of conductivity depending on R ions; that is, LaNiO_3 shows metallic conductivity at any temperature and the others with smaller R ions such as Pr, Nd or Sm exhibit transition from metallic to semiconducting or insulating with decreasing temperature [4,5]. The metal-semiconductor or insulator transition temperature increases with decreasing ionic radius of the rare earth [5].

The preparation of RNiO_3 meets some difficulties except R=La for the two reasons. First, since the formation of RNiO_3 from R_2O_3 and NiO involves the oxidation of nickel from Ni(II) to Ni(III) in a highly oxidized state, the preparation needs high oxygen pressure of 60 kbar and high temperature of 950

°C in order to promote the solid-state reaction [6]. Second, the perovskite structure (see Fig. 1) of RNiO_3 becomes more distorted with decreasing ionic radius of the rare earth from La to Lu. The distorted RNiO_3 needs to be stabilized by applying high pressure such as 60 kbar [6] during preparation, otherwise RNiO_3 would not be formed. Recently, Lacorre *et al.* [5] has reported that the use of nitrates as starting materials enables the preparation of RNiO_3 with R=La, Pr, Nd and Sm under relatively lower pressures of 150 - 200 bar at 1000 °C.

Instead of the high pressure and high temperature synthesis, the low-temperature processing, by which higher oxidation state of Ni can be attained, should be pursued to facilitate the preparation of RNiO_3 compounds. For example, Vassiliou *et al.* [7] prepared NdNiO_3 at 650 °C under 1 atm oxygen pressure using oxides dissolved in nitric acid or the gel powders derived from aqueous solutions of nitrates containing citric acid and ethylene glycol. They claimed that NdNiO_3 prepared by this method has a rhombohedrally distorted structure, which differs from an orthorhombic structure prepared at high pressure [5], and shows the metal-semiconductor (or insulator) transition at 130 K, which is lower than 200 K [5] of the orthorhombic NdNiO_3 . These discrepancies in the crystal structure and the electrical property, however, have not been explained clearly in their work.

In the preceding two chapters, it has been shown that the sol-gel process is very useful for the preparation of the superconducting oxides at lower temperatures under ambient pressure. It is of interest, therefore, to apply the sol-gel process to various oxides related to superconductors as the novel preparation method in searching for new superconducting materials. In this chapter, the sol-gel process has been applied to the preparation of NdNiO_{3-y} as

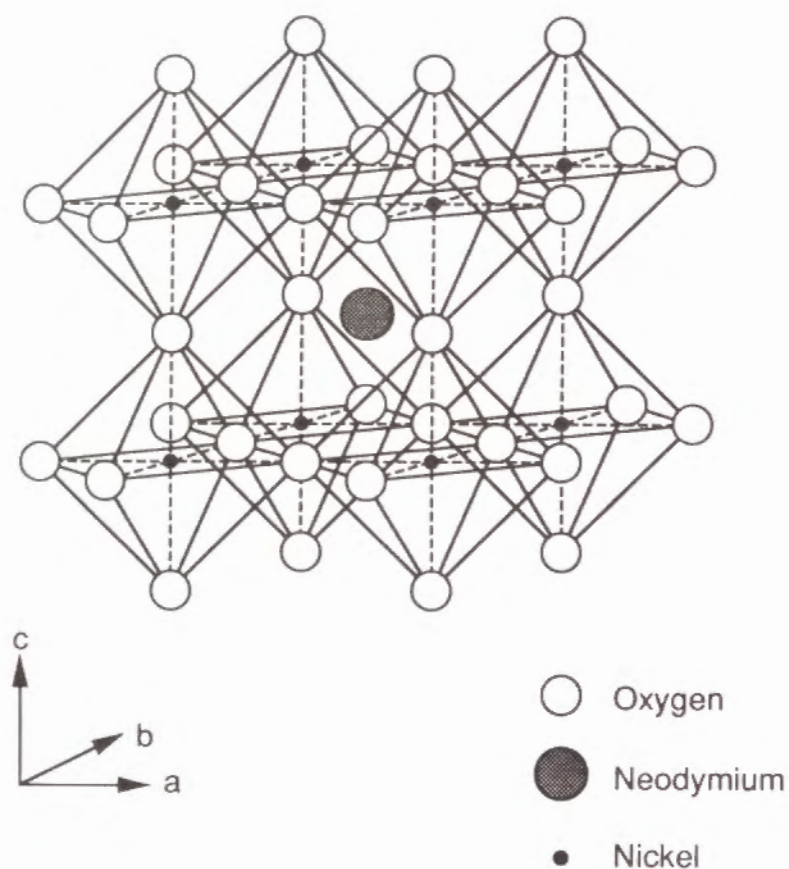


Fig. 1. The structure of NdNiO_3 .

a technique for the low-temperature process. The gels were obtained from aqueous solutions of metal acetates [8] prepared using ethylenediaminetetraacetic acid (EDTA) as a chelating agent. The substitution of Y for Nd was carried out in order to know the effect of the rare-earth ion size on the structure and properties of NdNiO_{3-y} . The differences in the structure and properties between the present samples and NdNiO_3 prepared at high pressure by Laccore *et al.* [5] were discussed in terms of the structure and oxygen deficiency.

2. EXPERIMENTAL

2.1. Preparation of Samples

Figure 2 shows the flow chart of the sol-gel processing in this work. Metal acetates $\text{Nd}(\text{CH}_3\text{COO})_3 \cdot \text{H}_2\text{O}$ (Wako Pure Chemical Industries, Osaka, Japan), $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$ (Mitsuwa Pure Chemicals, Osaka, Japan) and $\text{Ni}(\text{CH}_3\text{COO})_2$ (Wako Pure Chemical Industries) were used as starting materials. The metal acetate reagents were dissolved in distilled water to make an aqueous solution with cation molar ratio of $\text{Nd}:\text{Y}:\text{Ni}=(1-x):x:1$ ($x=0, 0.1, 0.2$). After adding EDTA, the solution was stirred for 2 h. The molar ratio of EDTA to nickel was fixed at $\text{EDTA}/\text{Ni}=1$. The resultant transparent solution in blue color was concentrated in an oven at 80°C for 3 days to be gelled. The transparent blue gels were pulverized using an agate mortar, heated to 700°C at a rate of $2.5^\circ\text{C}/\text{min}$ in air or O_2 , and kept there for 10 h to obtain the powder samples. The pulverized gels were heated to 400°C at a rate of $2.5^\circ\text{C}/\text{min}$ in air and kept there for 1 h, and the resultant black powders were ground, pressed into pellets of 13 mm diameter and about 1 mm thick under a pressure of 6 MPa, and heated at 700°C for 20 - 50 h in air or flowing oxygen at a

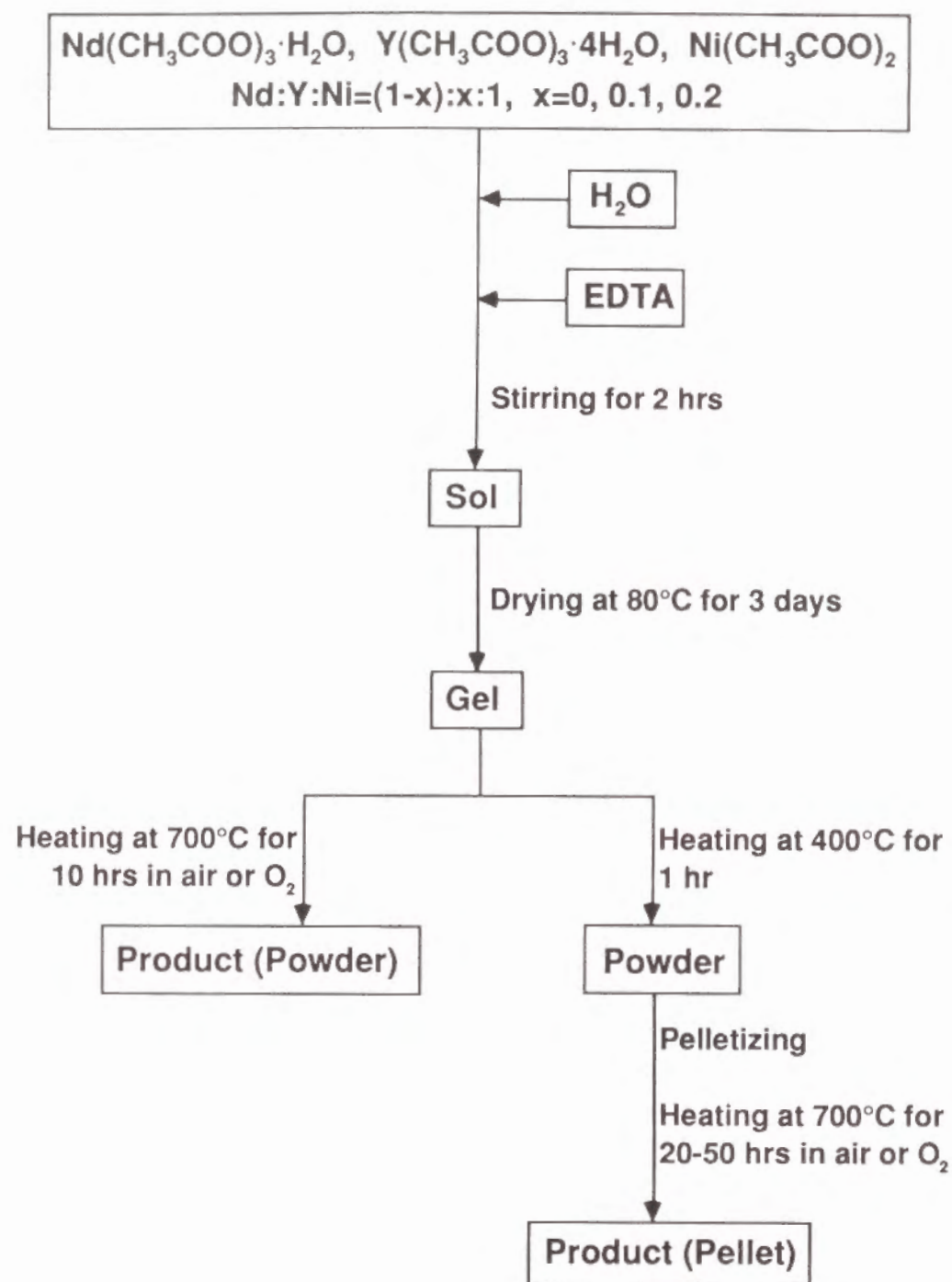


Fig. 2. The process for the synthesis of $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_3$ via the sol-gel method.

heating rate of 5 °C/min.

2.2. X-Ray Diffraction

The crystalline phases evolved in the heat-treated products were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ phases were determined by the XRD using Si powder as the internal standard substance.

2.3. Iodometric Titration

The formal valence of Ni in $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ was determined by the iodometric titration. The pulverized sample (approximately 0.050 g) was exactly weighed (W_i g) and covered with 1 g of KI powder in a beaker, to which 10 ml of 6 N HCl was added to make a solution. After adding 10 ml of distilled water and subsequently 20 ml of a buffer solution, which contains 116 g of $\text{CH}_3\text{COONH}_4$, 86 ml of CH_3COOH and water in a total volume of 500 ml, the resultant solution was titrated with a N/100 $\text{Na}_2\text{S}_2\text{O}_3$ standard solution until the yellow color of the solution vanished. During the titration the solution was purged with N_2 gas. Then 1 % aqueous solution of starch was added as indicator and the solution was successively titrated with the N/100 $\text{Na}_2\text{S}_2\text{O}_3$ standard solution (V_i l) until the violet color vanished. The formal valence of Ni^{2+p} in $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ was determined from the following equation,

$$p = \frac{(M - M_0)CV_i}{W_i - M_0CV_i} \dots (1)$$

where M is the molecular weight of $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_3$, M_0 is the atomic weight of

oxygen and C is the concentration of the $\text{Na}_2\text{S}_2\text{O}_3$ standard solution. The oxygen deficiency, y , was calculated from the equation, $y=(1-p)/2$, assuming that Nd, Y and O have the formal valence of +3, +3 and -2, respectively.

2.4. XPS Measurement

The x-ray photoelectron spectroscopy (XPS) measurement was performed for the pellet products using an ULVAC-PHI model 5500 spectrometer with $\text{MgK}\alpha$ radiation (15kV-27mA).

2.5. Electrical Resistance

The d.c. electrical resistance of the samples was measured by the four probe method at temperatures from 50 to 300 K with a Chino Instrument Company superconductivity test system. For this measurement, the rectangular samples were cut from pellets, with dimensions of roughly $13 \times 3 \times 1 \text{ mm}^3$.

3. RESULTS

3.1. Formation of the NdNiO_{3-y} Phases

The heating conditions and the crystalline phases precipitated in the gels are summarized in Table I. Figure 3 shows the XRD patterns of the powder samples obtained by heating the gel of NdNiO_3 composition at 700°C for 20 h in air or flowing O_2 . It is seen that the powder sample heated in air consists of NdNiO_{3-y} and NiO, and that heated in O_2 consists of NdNiO_{3-y} , Nd_2O_3 and NiO. Traces of Nd_2O_3 and NiO did not disappear even when heating time was prolonged up to 50 h. Both of the pellet samples heated in air and flowing oxygen, on the other hand, are the single-phase NdNiO_{3-y} as seen in Fig. 4.

Table I The heating condition and the precipitated crystalline phases in the $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ samples. Samples of nos.1 and 2 are powders and those of nos. 3 - 6 are pellets.

Sample No.	x	Heating Condition	Crystalline Phases
1	0	700°C , 20h, air	NdNiO_{3-y} , NiO
2	0	700°C , 20h, O_2	NdNiO_{3-y} , Nd_2O_3 , NiO
3	0	$(400^\circ\text{C}, 1\text{h}, \text{air}) \rightarrow (700^\circ\text{C}, 20\text{h}, \text{air})$	NdNiO_{3-y}
4	0	$(400^\circ\text{C}, 1\text{h}, \text{air}) \rightarrow (700^\circ\text{C}, 20\text{h}, \text{O}_2)$	NdNiO_{3-y}
5	0.1	$(400^\circ\text{C}, 1\text{h}, \text{air}) \rightarrow (700^\circ\text{C}, 20\text{h}, \text{O}_2)$	$\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$
6	0.2	$(400^\circ\text{C}, 1\text{h}, \text{air}) \rightarrow (700^\circ\text{C}, 20\text{h}, \text{O}_2)$	$\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$, Nd_2O_3 , NiO

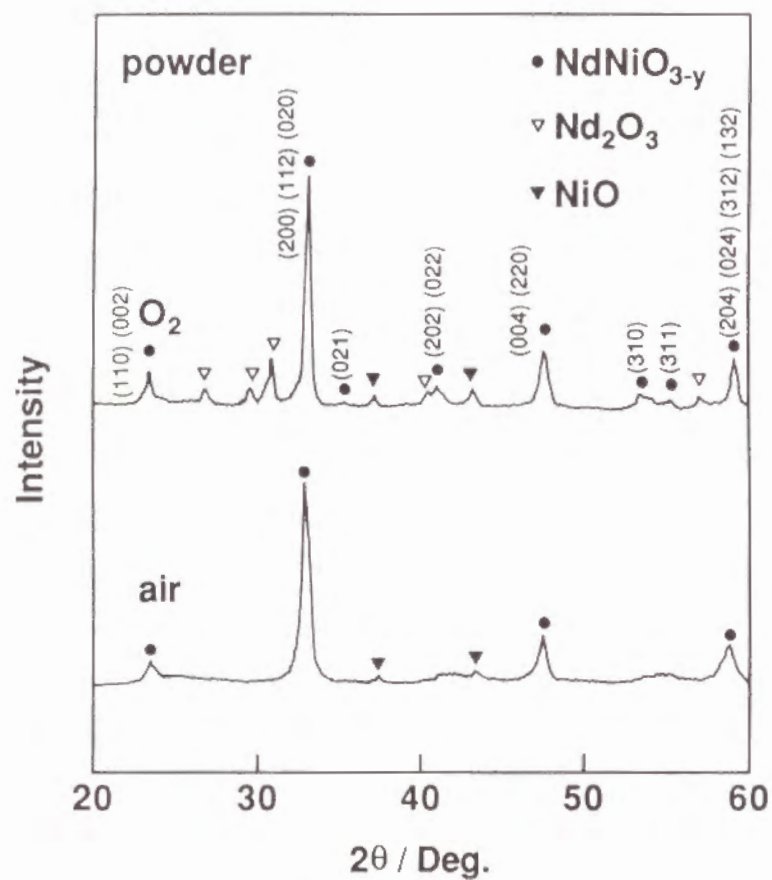


Fig. 3. The XRD patterns of the powders obtained by heating the gel with the NdNiO_3 composition at 700 °C for 20 h in O_2 or air.

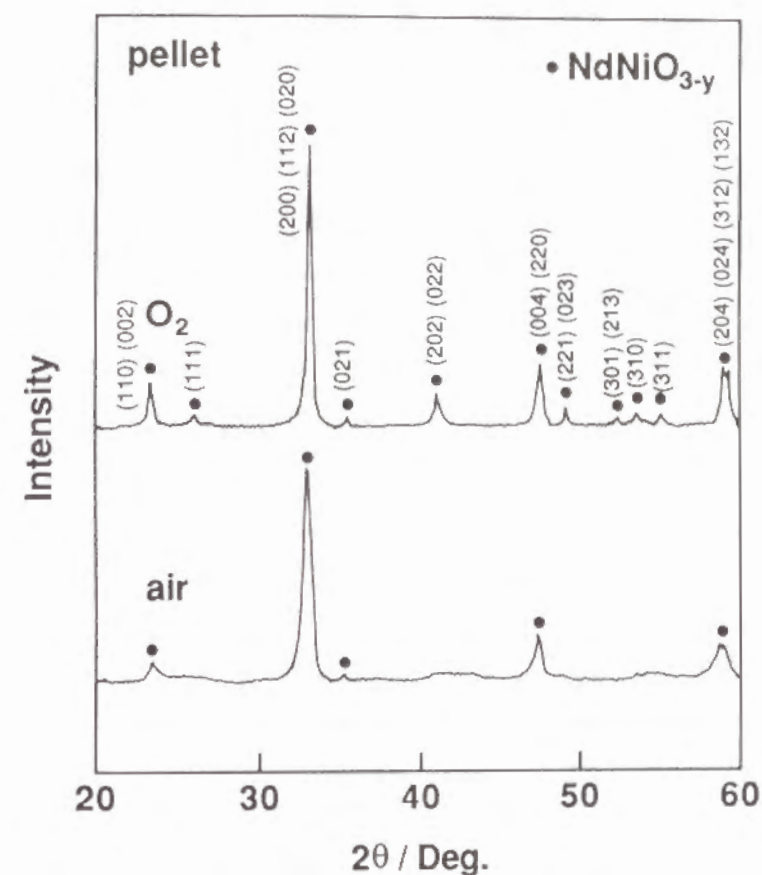


Fig. 4. The XRD patterns of the pellets obtained by sintering the heat-treated gel with the NdNiO_3 composition at 700 °C for 20 h in O_2 or air.

Figure 5 shows the XRD patterns of the pellet samples $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ ($x=0.1, 0.2$) heated at 700 °C for 20 h in flowing oxygen. The pattern of the sample of $x=0.1$ shows the single-phase $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ with perovskite structure while that of $x=0.2$ shows the presence of three phases, Nd_2O_3 , NiO and $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$.

3.2. Crystal Structure

The presence of the peaks near 26°, 35° and 49° in the diffraction pattern of the perovskite NdNiO_{3-y} (Fig. 4) evidently indicates that the present NdNiO_{3-y} has an orthorhombic form like NdNiO_3 prepared at high pressure by Lacorre *et al.* [5]. It should be noted that these peaks are absent in the rhombohedral NdNiO_3 prepared from gels under 1 atm oxygen by Vassiliou *et al.* [7]. The discrepancy in crystal structure between the present sample and the sample of Vassiliou *et al.* may arise from the different oxygen contents as mentioned below. The lattice constants a , b and c are summarized in Table II for NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ prepared in this work and those of NdNiO_3 prepared under high pressure of 150 - 200 bar [5]. The values of $a=0.5397$ nm, $b=0.5396$ nm and $c=0.7627$ nm of NdNiO_{3-y} prepared in the present work are somewhat larger than those of NdNiO_3 prepared under high pressure which exhibits $a=0.53888$ nm, $b=0.53845$ nm and $c=0.76127$ nm. $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ exhibits $a=0.5394$ nm, $b=0.5393$ nm and $c=0.7618$ nm, which are all smaller than those of the non-substituted NdNiO_{3-y} . This is attributed to a decrease in the average ionic radius of the rare earth due to the substitution of the smaller Y ions for Nd.

3.3. Valence of Nickel and Oxygen Deficiency

The values of y , which correspond to the oxygen deficiency, in the

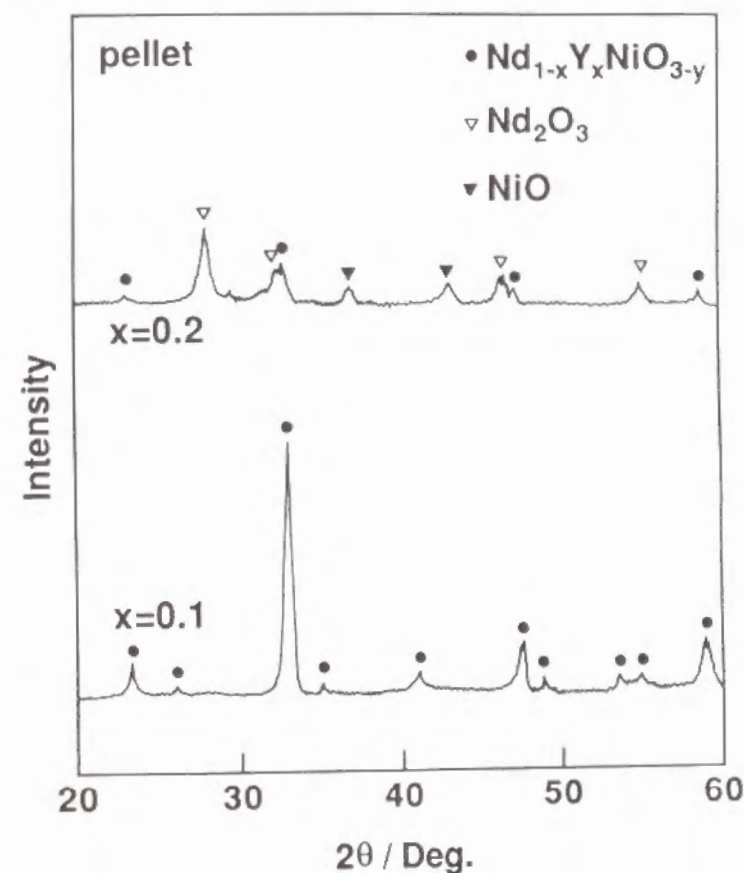


Fig. 5. The XRD patterns of the pellets obtained by sintering the heat-treated gel with the $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_3$ composition of $x=0.1$ and 0.2 at 700 °C for 20 h in O_2 or air.

Table II The lattice constants and the oxygen deficiency of $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$.

Sample	Lattice Constants / nm			y	Ref.
	a	b	c		
NdNiO_3	0.53888	0.53845	0.76127	-	Lacorre <i>et al.</i> [5]
NdNiO_3^*	0.540	-	-	-	Vassiliou <i>et al.</i> [7]
NdNiO_{3-y}	0.5397	0.5396	0.7627	0.24	this work(No. 4)
$\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$	0.5394	0.5393	0.7618	0.23	this work(No. 5)

*Rhombohedral unit cell, $\alpha=60.5^\circ$

NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ samples are determined to be 0.24 and 0.23, respectively, from the iodometric titration. Consequently, the present NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ can be described as $\text{Nd}(\text{Ni}^{2+}_{0.48}\text{Ni}^{3+}_{0.52})\text{O}_{2.76}$ and $\text{Nd}_{0.9}\text{Y}_{0.1}(\text{Ni}^{2+}_{0.46}\text{Ni}^{3+}_{0.54})\text{O}_{2.77}$, respectively, in which almost a half of Ni^{3+} ions of the stoichiometric NdNiO_3 is reduced to Ni^{2+} ions.

Figure 6 shows the XPS spectrum of $\text{NdNiO}_{2.76}$ in the region from 850.0 to 869.0 eV. The binding energy has been calibrated with the C1s peak at 284.6 eV. The observed Ni 2p_{3/2} peak can be resolved into two components separated by 2.5 eV, suggesting that two species of Ni ions coexist in the present sample. The peak position of the higher-energy component at 855.5 eV agrees well with that of Ni^{3+} reported previously [9,10]. The peak at around 853.5 eV can be assigned to Ni^{2+} , noting that the binding energy of Ni^{2+} in NiO is 853.5-854.0 eV [9]. The $\text{Ni}^{3+}/\text{Ni}^{2+}$ abundance is calculated to be 52 % for Ni^{3+} and 48 % for Ni^{2+} from the ratio of the peak area, which is in excellent agreement with the result of the iodometric titration.

3.4. Electrical Properties

The resistivity of both $\text{NdNiO}_{2.76}$ and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$ was approximately 0.10 $\Omega\text{-cm}$ at room temperature. Figure 7 shows the temperature dependence of the electrical resistance of the samples. On cooling, $\text{NdNiO}_{2.76}$ exhibits metallic conductivity with $dR/dT > 0$, where R is the resistance and T is the absolute temperature, in the range between 300 and 130 K, and the conducting behavior turns into semiconducting at temperatures lower than 130 K. On heating, semiconduction is maintained up to 180 K with larger values of resistance than that on cooling, and at temperatures higher than 180 K the resistance exactly coincides with that on cooling, showing a large hysteresis in one cycle of a

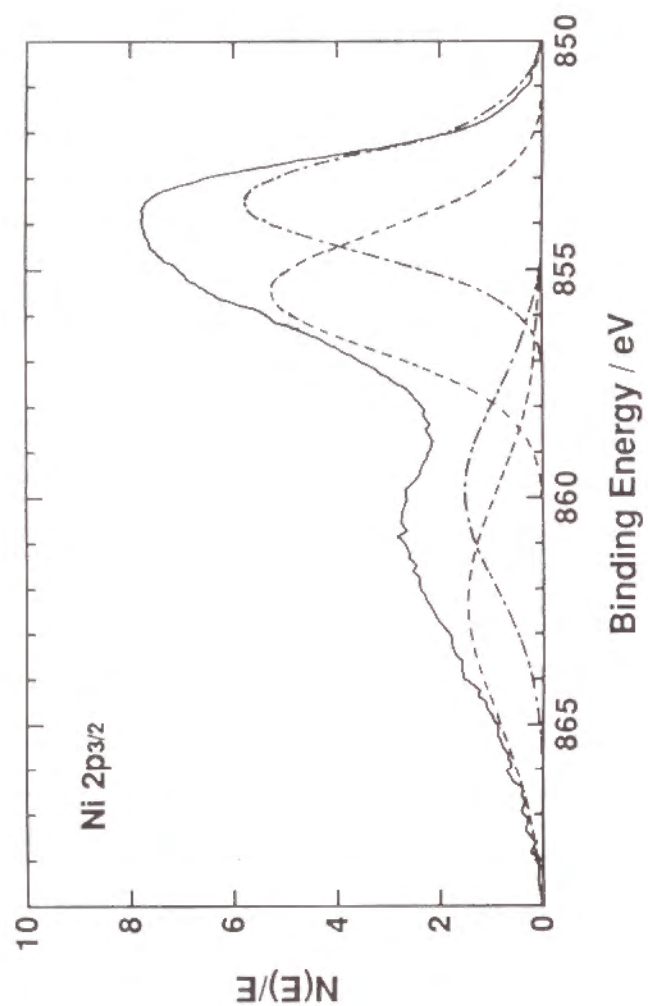


Fig. 6. The XPS spectrum of $\text{NdNiO}_{2.76}$ in the region of $\text{Ni } 2p_{3/2}$.

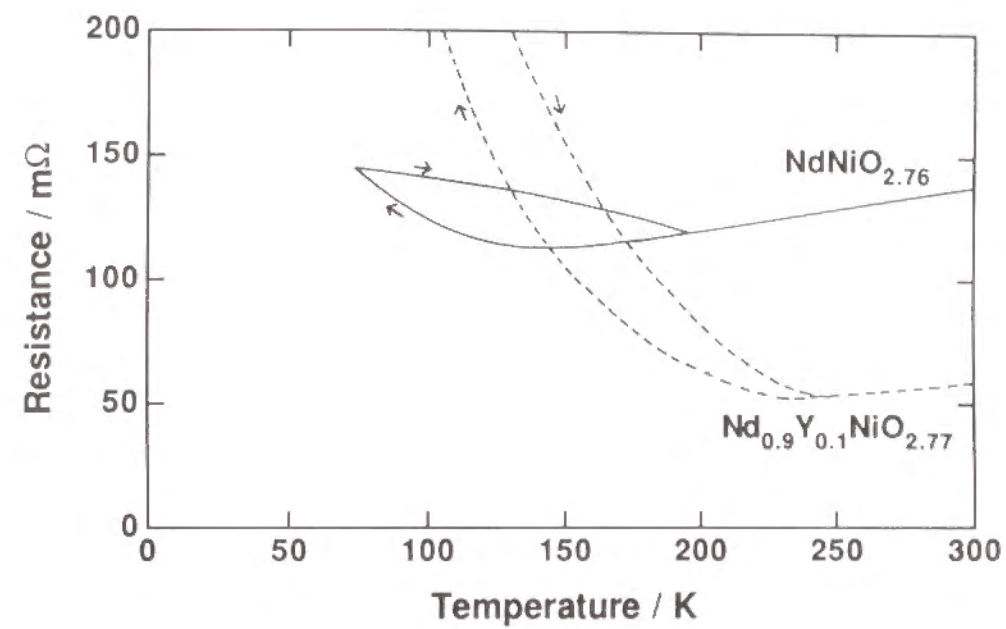


Fig. 7. Temperature dependence of the electrical resistance of $\text{NdNiO}_{2.76}$ and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$.

thermal pattern of the resistance. The resistance of $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$ decreases from room temperature to 240 K and then increases with decreasing temperature as shown in Fig. 7. On heating, the resistance is larger than that on cooling below 240 K and coincides with that above 240 K.

4. DISCUSSION

4.1. Rapid Formation of the NdNiO_{3-y} phases from the gels

The present preparation method can produce a single-phase NdNiO_{3-y} in relatively short heating time of 20 h compared with that of 120 h employed previously by Vassiliou *et al.* [7]. It should be emphasized that the single-phase NdNiO_{3-y} can be obtained by heating in air, which is less oxidizing condition than in O_2 atmosphere, although the crystallinity is lower in air than in oxygen atmosphere. Therefore, it can be said that the high reactivity of the starting materials, which is attributed to the homogeneous distribution of Nd and Ni ions in the gel, makes it possible to obtain NdNiO_{3-y} under ambient pressure in short time.

4.2. Effect of Substitution of Y for Nd on the Crystal Structure

The formation of the perovskite phase is considerably suppressed in the Y-substituted sample of $x=0.2$ in $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ as seen in Fig. 5, which is probably caused by the restriction of the ionic radius at the rare earth site. That is, the average ionic radius of " $\text{Nd}_{0.8}\text{Y}_{0.2}$ " is too small to form a stable perovskite structure. The tolerance factors of the three crystals, NdNiO_3 , $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_3$ and $\text{Nd}_{0.8}\text{Y}_{0.2}\text{NiO}_3$, which are defined as $t=(r_{\text{R}}+r_{\text{O}})/\sqrt{2}(r_{\text{Ni}}+r_{\text{O}})$ where r_{R} , r_{Ni} and r_{O} are the effective ionic radius of rare earth, nickel and oxygen, respectively,

are calculated to be 0.97, 0.96 and 0.95, respectively, using Shannon's ionic radius data ($r_{\text{Nd}}=0.127$, $r_{\text{Y}}=0.1075$, $r_{\text{Ni}}=0.056$ and $r_{\text{O}}=0.135$ nm) [11]. It is considered that a boundary lies between $t=0.96$ and 0.95, below which RNiO_3 is not formed under ambient pressure.

4.3. Effect of Oxygen Deficiency on the Crystal Structure

The formation of oxygen vacancies and, accordingly, that of Ni^{2+} ions affects the crystal structure. It is thought that the bond length of $\text{Ni}^{3+}-\text{O}^{2-}$ is shorter than that of $\text{Ni}^{2+}-\text{O}^{2-}$ because of the higher oxidation state of nickel ion in the former, which explains the difference in the lattice constants between the present NdNiO_{3-y} and the NdNiO_3 prepared by Lacorre *et al.* [5]. The coordination state around nickel ions should be changed by the formation of oxygen defects; that is, a part of Ni^{2+} ions are bonded to oxygens less than six, probably forming the Ni^{2+}O_4 square plane which is a stable form because of the d^8 electronic configuration of Ni^{2+} .

4.4. Electrical Properties of the NdNiO_{3-y} Phases

The temperature dependence of resistance of the oxygen-deficient $\text{NdNiO}_{2.76}$ nearly agrees with that observed in NdNiO_3 prepared by Vassiliou *et al.* [7] with low-temperature method, but differs from the result of NdNiO_3 prepared at high pressure [5], which showed the metal-semiconductor (M-S, hereafter) transition at a higher temperature of 200 K. This discrepancy is attributed to the difference in the lattice constants and/or the oxygen content due to different preparation methods.

The occurrence of the thermal hysteresis of the resistance can be related to possible structural transition at the M-S transition. Lacorre *et al.* [5] has

reported that PrNiO_3 and NdNiO_3 show abrupt change in the unit cell volume near the M-S transition temperature. Also in the present case it is possible that this structural change occurs upon cooling and the low-temperature structure is frozen upon heating at temperatures over the M-S transition, resulting in the thermal hysteresis of the resistance.

The occurrence of the M-S transition is explained in terms of the band structure. Figure 8 shows the schematic model of the band structure around Fermi level for NdNiO_3 . The metallic conduction of NdNiO_3 is caused by the overlap of the unoccupied Ni-3d and occupied O-2p bands, of which the bandwidth varies with temperature and/or structure. According to Torrance *et al.* [12], the conducting behavior of RNiO_3 is dependent on the Ni-O-Ni bond angle. As the Ni-O-Ni angle becomes smaller by decreasing ionic radius of R, the bandwidth becomes narrower and the overlap of the Ni-3d and O-2p bands becomes smaller, eventually resulting in the formation of a charge transfer gap between Ni-3d and O-2p bands to change the conduction from metallic to semiconducting. The Ni-O-Ni bond angle can be changed also by temperature; that is, the decrease in temperature makes the Ni-O-Ni angle smaller. Therefore, the bandwidth becomes narrower with decreasing temperature, which results in the M-S transition. The present $\text{NdNiO}_{2.76}$ should have the larger Ni-O-Ni angle to make the bandwidth larger compared to NdNiO_3 prepared at high pressure because of the larger lattice constants of the former as mentioned in 3.2. This well explains the lower M-S transition temperature of the present $\text{NdNiO}_{2.76}$.

The substitution of Y for Nd clearly exhibits the size effect of R ions on the M-S transition; that is, $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$ exhibits the considerably higher M-S transition temperature of 240 K than $\text{NdNiO}_{2.76}$ with 130 K as seen in Fig. 7. In addition, the rate of increase in the resistance after the M-S transition

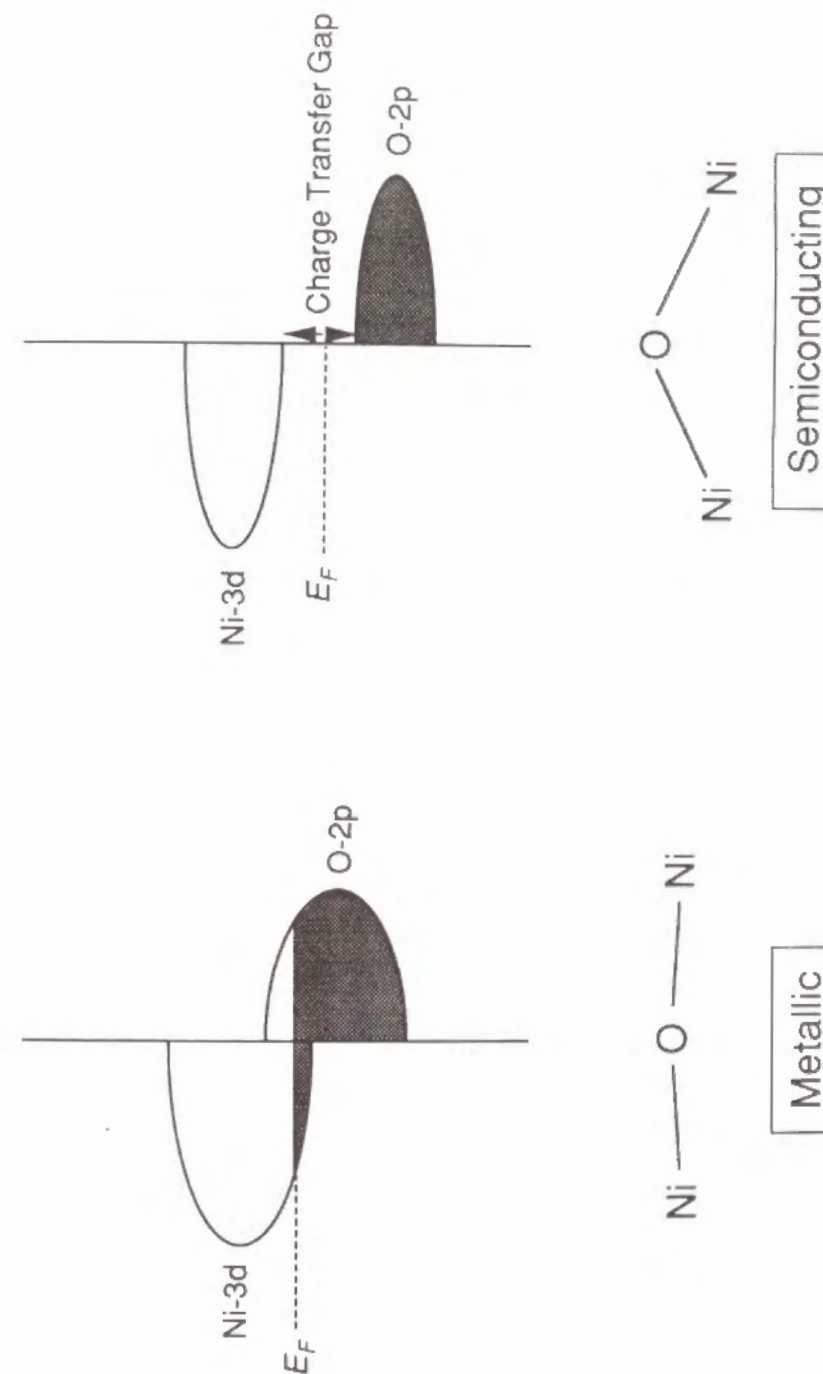


Fig. 8. The band structure of NdNiO_3 depending on the Ni-O-Ni angle.

with decreasing temperature is much larger in $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$ than in $\text{NdNiO}_{2.76}$. These results are attributed to the smaller lattice constants of $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{2.77}$ than those of $\text{NdNiO}_{2.76}$, which causes more bent Ni-O-Ni bond and hence the narrower bandwidth.

5. CONCLUSION

The oxygen-deficient NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ with a perovskite structure were prepared under ambient pressure by the sol-gel method starting with metal acetates, EDTA and water. A single-phase NdNiO_{3-y} was obtained in relatively short time of 20 h by heating at 700 °C in flowing oxygen or air. $\text{Nd}_{1-x}\text{Y}_x\text{NiO}_{3-y}$ was obtained as a single phase at $x=0.1$ but did not form at $x=0.2$. The amount of oxygen defects, y , was calculated to be 0.24 for NdNiO_{3-y} and 0.23 for $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$. The XPS measurement on Ni evidenced the mixed valence state of $\text{Ni}^{2+}/\text{Ni}^{3+}$ in the sample. The temperature dependent metal-semiconductor transition was observed at 130 and 240 K for NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$, respectively. The increase in the metal-semiconductor transition temperature by the substitution of Y for Nd is attributed to the decrease in the lattice constants, which results in the more bent Ni-O-Ni bond and hence the narrower bandwidth of Ni-3d and O-2p bands.

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CHAPTER 4

EFFECTS OF SUBSTITUTION OF SULFUR FOR OXYGEN ON THE STRUCTURE AND PROPERTIES OF $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ SUPERCONDUCTOR

INTRODUCTION

Partial substitution of elements in the known high-temperature superconducting oxides is one of the informative ways of studying the superconducting mechanism and is also a way of searching for new superconducting materials. Although there have been many studies on the chemical substitution of cations in superconducting oxides, few works have been aimed at the substitution of anions for oxygen ions.

Introduction of chalcogenide anions into the known superconducting oxides is of interest in that these anions may change the crystal structure due to their larger ionic radius than oxygen, without changing the apparent valence state in anion sites. In addition, change in the electronic structure is also expected as estimated by Adachi and Takano [1]; they have studied the electronic state of CuO_4^{6-} , CuS_4^{6-} and CuSe_4^{6-} clusters by DV- $X\alpha$ method, concluding that overlap of S-3p or Se-4p band and Cu-3d band is larger than that of O-2p band and

Cu-3d band, which indicates that covalency in CuS_4^{6-} or CuSe_4^{6-} is larger than that in CuO_4^{6-} cluster.

In this chapter, the effects of the substitution of sulfur for oxygen on the structure and properties of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system are discussed. In Section 1, the effects of sulfur substitution on the superconducting $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ are described. In Section 2, the non-superconducting $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_4$ undergo the sulfur substitution.

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SECTION 1 EFFECTS OF SULFUR SUBSTITUTION ON SUPERCONDUCTING $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$

1. INTRODUCTION

$\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, which is a K_2NiF_4 -type superconducting oxide, is an ideal material for studying the mechanism of high-temperature superconductivity because of its simple structure (see Fig.1), an easy formation of a single phase and a wide range of solid solutions [1]. It has been reported that the electrical properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ vary with the Sr concentration x from Mott insulator for $0 \leq x \leq 0.06$ to superconductor for $0.06 \leq x \leq 0.26$ to normal metal for $0.26 \leq x$ [1]. This variety of the electrical behavior is considered to be related to the change of the electronic interaction between Cu-3d and O-2p bands with varying hole concentration in the CuO_2 plane.

As estimated by Adachi and Takano [2,3], the overlap of S-3p and Cu-3d bands is larger than that of O-2p and Cu-3d bands. Therefore, it is interesting to investigate how the structure and properties of superconducting oxides change by replacing oxygen with sulfur. Kambe and Kawai [4] have shown that incorporation of a small amount of sulfur in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ results in the formation of phases having much shorter lattice constants along c -axis, a slightly higher T_c and a sharper superconducting transition. Taylor *et al.* [5] have shown that 10 % replacement of CuO with CuS in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ gives rise to a superconducting transition at 108 K. Substitution of sulfur for oxygen, however, has not been carried out in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor.

In this work, effects of the substitution of sulfur for oxygen on the

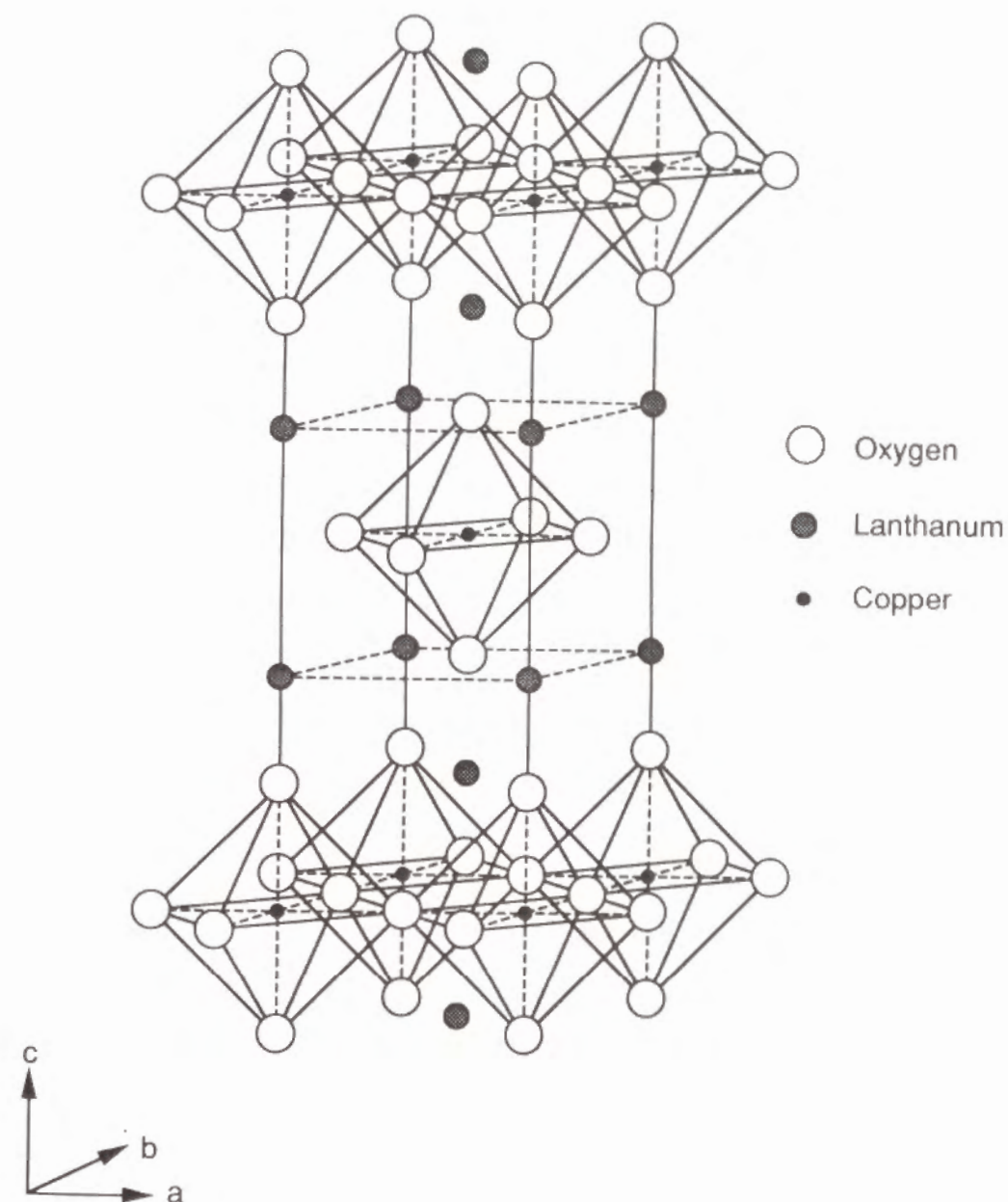


Fig. 1. The structure of La_2CuO_4 .

structure and electrical properties of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$, which shows the highest superconducting transition temperature in the La-Sr-Cu-O system [1], have been investigated.

2. EXPERIMENTAL

2.1. Sample Preparation

A series of ceramic pellets of nominal compositions $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ ($y=0, 0.05, 0.10, 0.13, 0.15, 0.20, 0.30, 0.40, 0.50$) were prepared by the solid-state reaction using high-purity reagent-grade La_2O_3 (Wako Pure Chemical Industries, Osaka, Japan), SrCO_3 (Nacalai Tesque, Kyoto, Japan), CuO (Kanto Chemical, Tokyo, Japan) and CuS (Nacalai Tesque). The chemicals were mixed and calcined by heating to 900 °C at a rate of 5 °C/min and being kept there for 5 h in air. The calcined powder mixture was ground and pressed into pellets of 20 mm diameter and 1-1.5 mm thick, and heated to 1000 °C at a rate of 5 °C/min, kept there for 10 h in air and cooled slowly in the furnace to room temperature.

2.2. X-Ray Analysis

Crystalline phases of the products were identified by the powder x-ray diffraction (XRD) method with a Rigaku Denki Company model RAD-IIA diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the crystals were determined by the internal standard method using Si or Ge as references. The sulfur content in the products was determined by the x-ray fluorescence analysis using a Rigaku Denki Company model KG-4 x-ray fluorescence analyzer.

2.3. Electrical Resistance and Magnetic Susceptibility

The d.c. electrical resistance of the samples was measured at temperatures from 300 K to 28 K by a four-probe method using a Chino Instrument company superconductivity test system. The a.c. magnetic susceptibility of the samples was measured from 300 K to 28 K by the Hartshorn bridge method with a frequency of 270 Hz and an amplitude of 100 mV.

3. RESULTS

3.1. Phase Analysis

Figure 2 (a) - (c) show the XRD patterns of the products with varying sulfur content. It can be seen that crystals of K_2NiF_4 structure are obtained as a single phase for $y_{\text{cal}} \leq 0.20$. For higher sulfur contents, $y_{\text{cal}} > 0.20$, however, additional peaks of $\text{La}_2\text{O}_2(\text{SO}_4)$ and unknown phases appear in the diffraction patterns and they grow with increasing sulfur content.

3.2. Sulfur Content

The sulfur content was analyzed for the heat-treated products whose calculated sulfur content y_{cal} is not larger than 0.20, and which were obtained as single-phase materials. The analyzed sulfur contents y_{ana} are plotted against the calculated sulfur content y_{cal} in Fig. 2, and are summarized in Table I. It is seen that more than 60 - 70 % of sulfur in the starting powder mixture is left in the heating products. The analyzed sulfur content y_{ana} is represented by "y" hereafter.

3.3. Crystal Structure

The crystal structure at room temperature changes from tetragonal to orthorhombic as the sulfur content increases, which is evidenced by the appearance

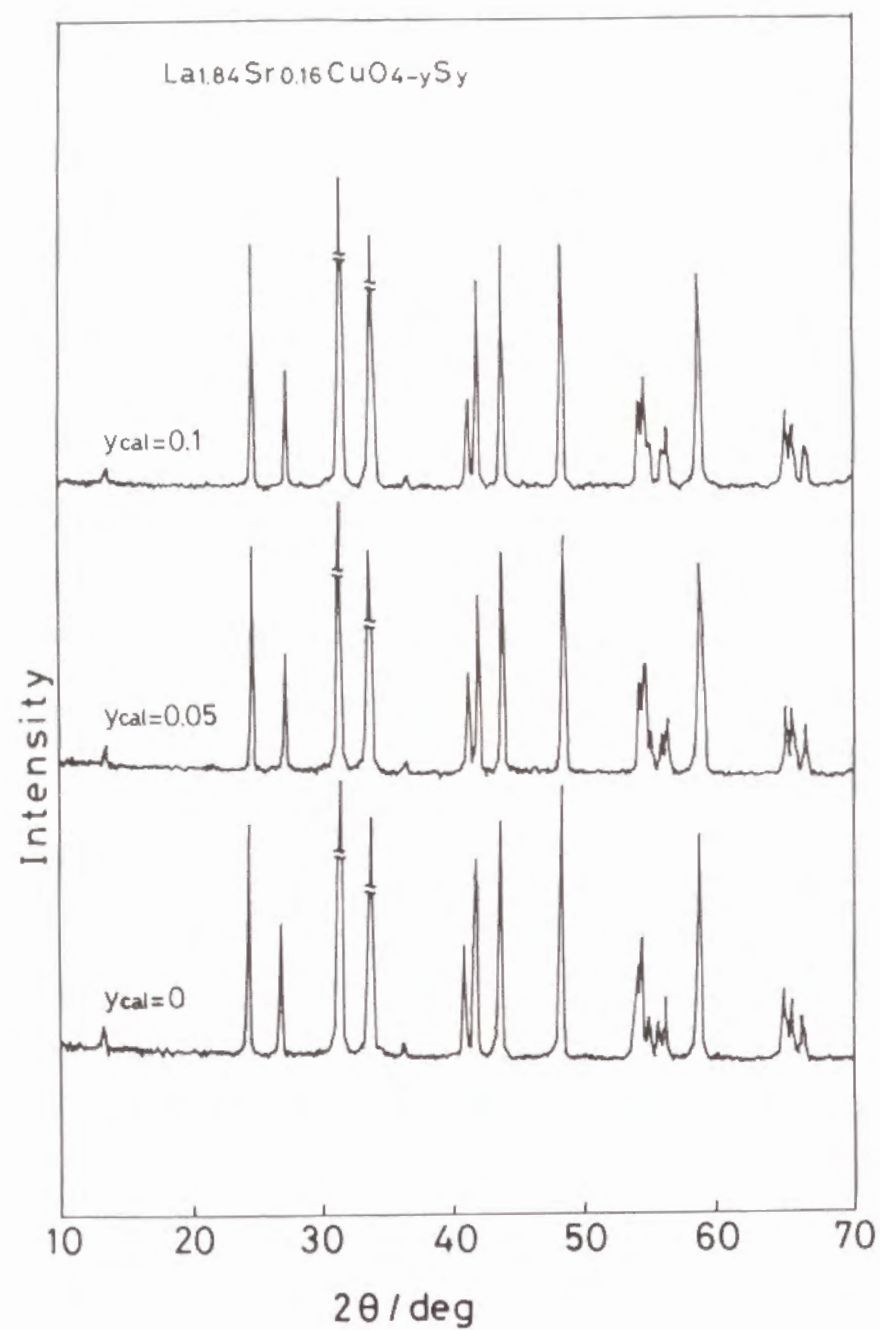


Fig. 2. (a) The XRD patterns of the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ samples with the calculated sulfur content, y_{cal} , of 0, 0.05 and 0.1.

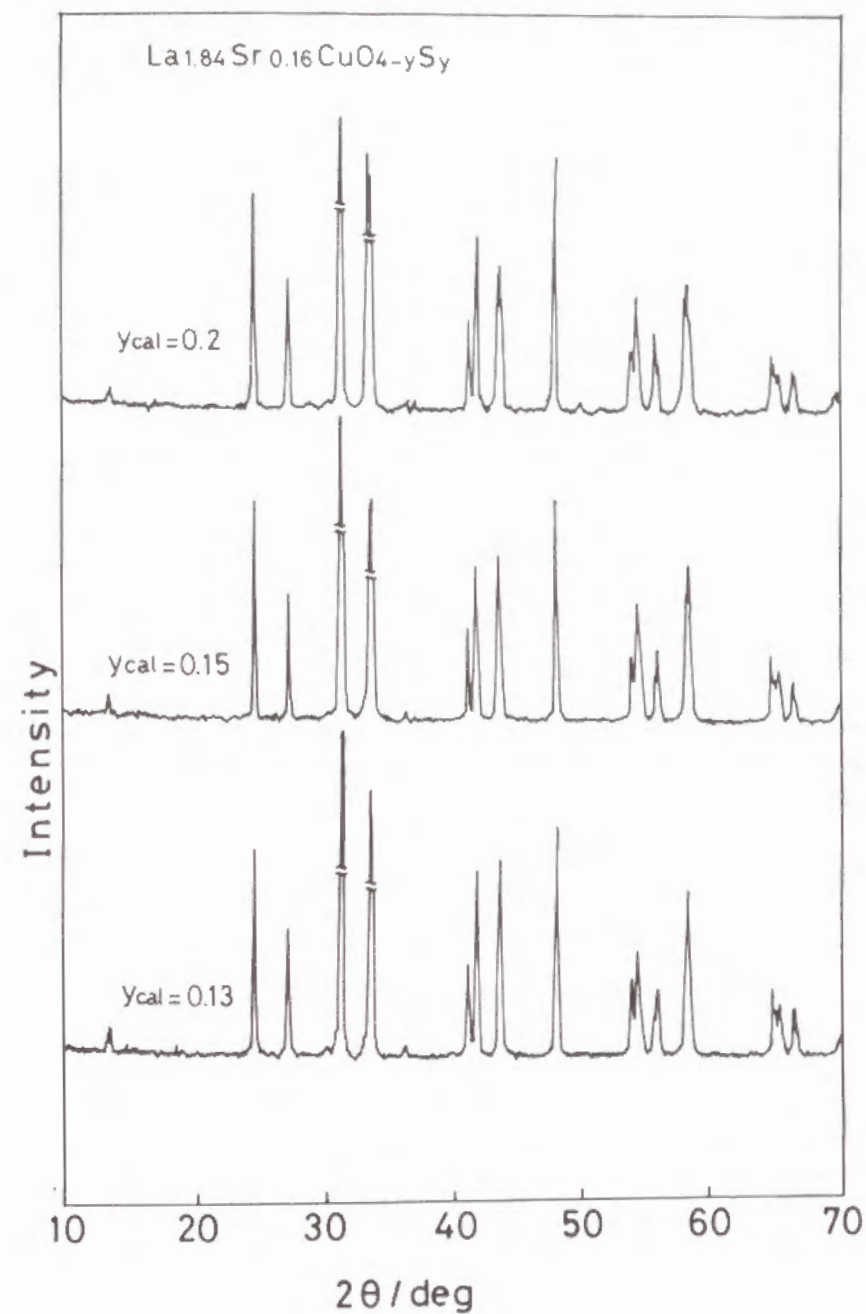


Fig. 2. (b) The XRD patterns of the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ samples with the calculated sulfur content, y_{cal} , of 0.13, 0.15 and 0.2.

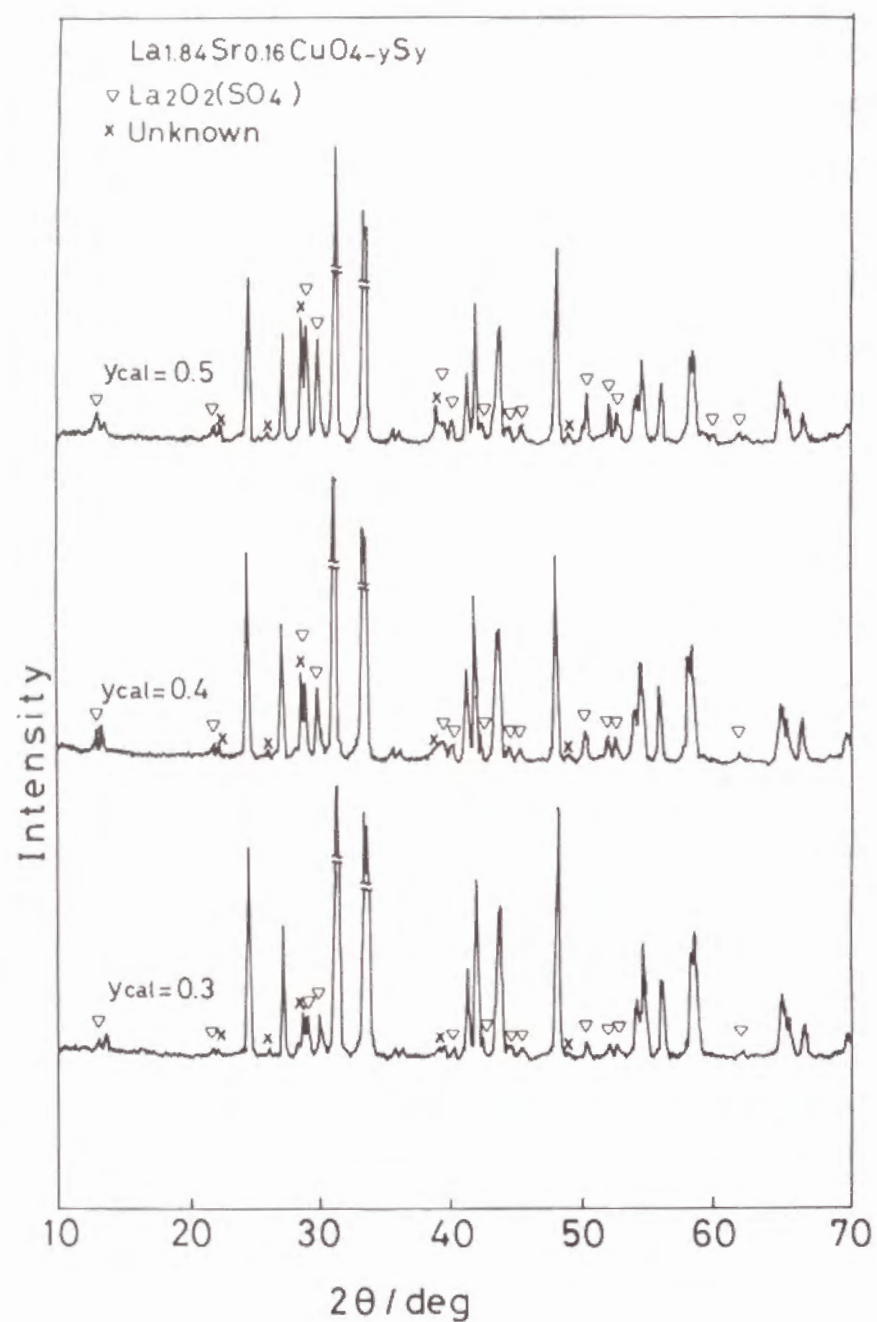


Fig. 2. (c) The XRD patterns of the La_{1.84}Sr_{0.16}CuO_{4-y}S_y samples with the calculated sulfur content, y_{cal} , of 0.3, 0.4 and 0.5.

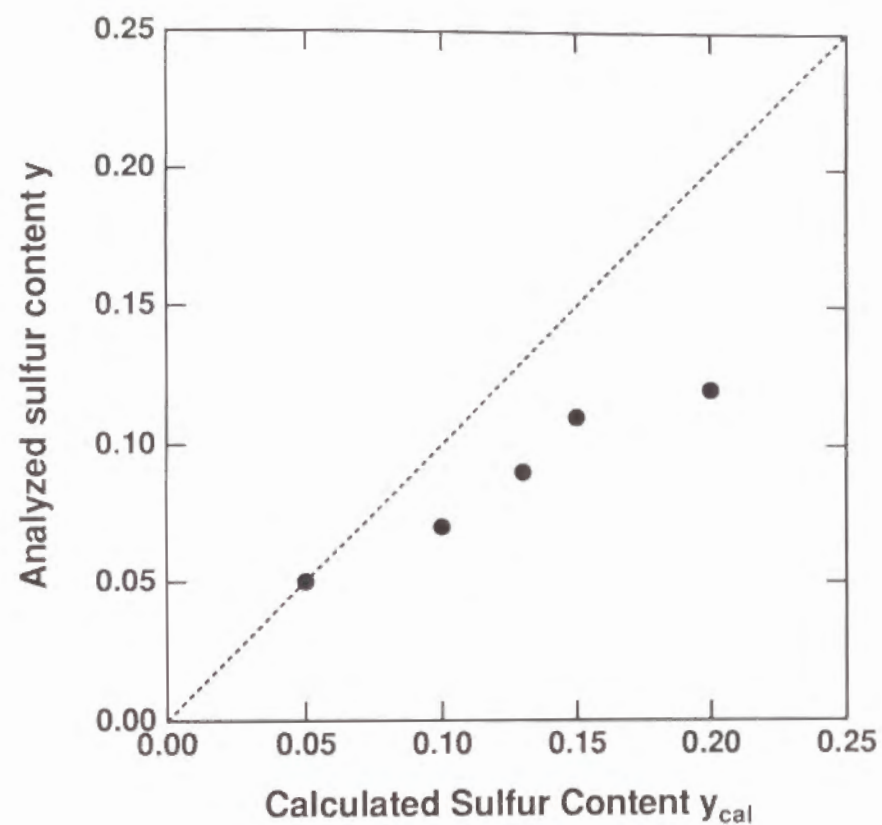


Fig. 3. Relation between the analyzed sulfur content and the calculated sulfur content in La_{1.84}Sr_{0.16}CuO_{4-y}S_y.

Table I The calculated and the analyzed sulfur content of the single-phase $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$.

Calculated Sulfur Content	Analyzed Sulfur Content
y_{cal}	y_{ana}
0	0
0.05	0.05
0.10	0.07
0.13	0.09
0.15	0.11
0.20	0.12

of the diffraction peak splitting; that is, the (110) peak of the tetragonal phase is split into the (200) and (020) peaks of the orthorhombic phase for $y_{\text{cal}} > 0.15$. Figure 4 shows the sulfur content dependence of the in-plane lattice constants, namely a for the tetragonal unit cell and a and b for the orthorhombic unit cell. As can be seen in the figure, $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ is tetragonal for $y \leq 0.09$ and orthorhombic for $y > 0.09$. The lattice constant a increases with increasing sulfur content in the range $y \leq 0.09$, where the tetragonal phase is found. The lattice constant a decreases once upon the appearance of the orthorhombic phase at y equaling 0.11 and then increases again at about $y = 0.12$ in the single-phase range. The lattice constant b increases with increasing sulfur content in the range $0.11 \leq y < 0.30$ where the orthorhombic phase is found as the single phase. At $y > 0.30$, the lattice constants a and b of the crystals almost invariant within the experimental error. Extrapolation of the lattice constants to the lower sulfur content, where the crystal phase is single, indicates that the solubility limit is located around $y = 0.13$.

Dependence of the lattice constant c on the analyzed sulfur content y is shown in Fig. 5. A monotonical decrease in the lattice constant with increasing sulfur content is observed.

The values of the lattice constants are summarized in Table II. The largest deviation of the lattice constants from those of the undoped crystal is about +0.3 % for the in-plane lattice constant a and -0.5 % for the lattice constant c .

3.4. Electrical Resistance

Figure 6 shows the temperature dependence of the d.c. electrical resistance of sulfur-doped samples. The superconducting transition temperatures of these

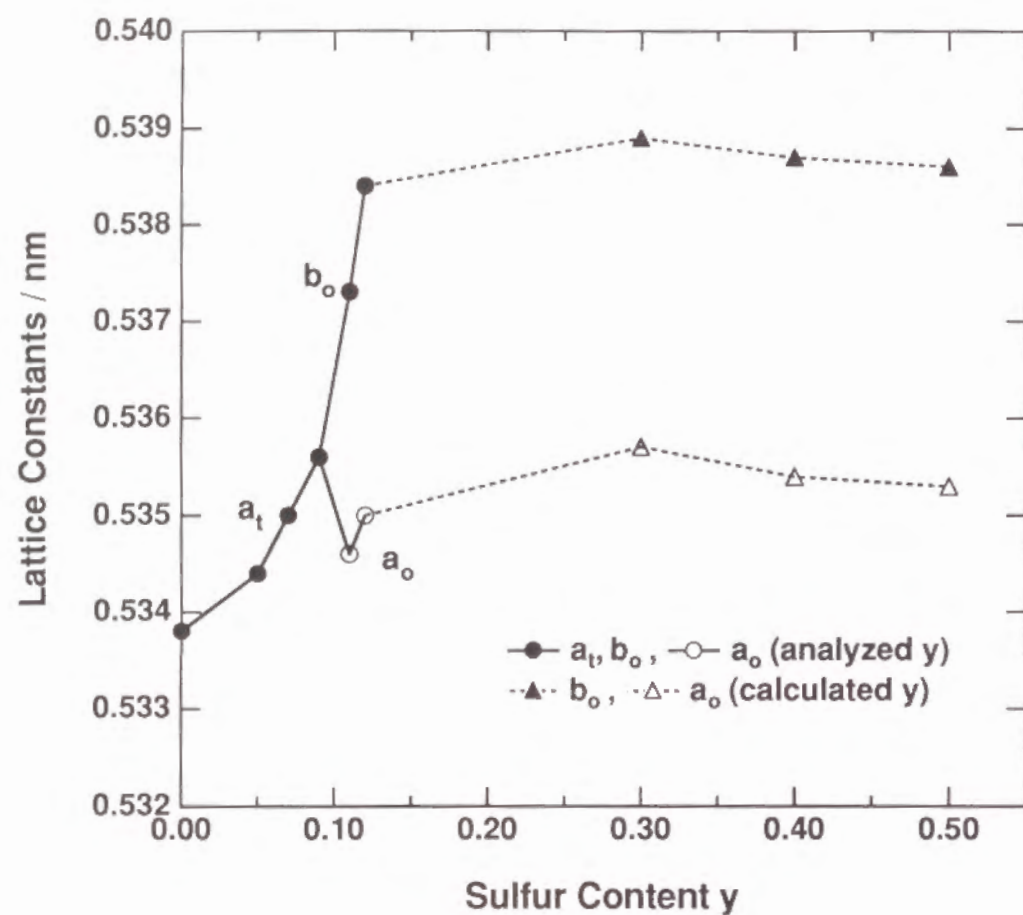


Fig. 4. Dependence of the lattice constants on the sulfur content y in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$. The " a_t " represents the tetragonal unit cell and the " a_o " and " b_o " represent the orthorhombic unit cell.

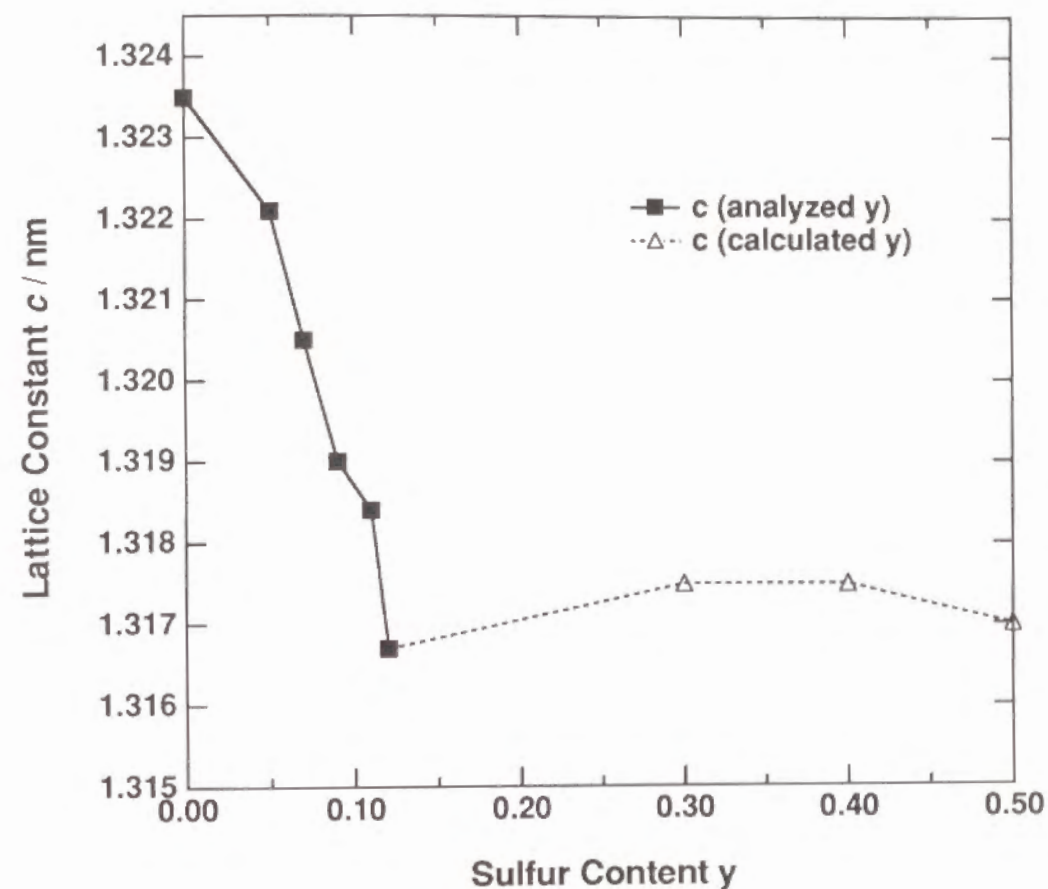


Fig. 5. Dependence of the lattice constant c on sulfur content.

Table II Lattice constants of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$.

Sulfur Content		Lattice Constants / nm		
y_{ana}	y_{cal}	a	b	c
0		0.5338	-	1.3235
0.05		0.5344	-	1.3221
0.07		0.5350	-	1.3205
0.09		0.5356	-	1.3190
0.11		0.5346	0.5373	1.3184
0.12		0.5350	0.5384	1.3167
	0.3	0.5357	0.5389	1.3175
	0.4	0.5354	0.5387	1.3175
	0.5	0.5353	0.5386	1.3170

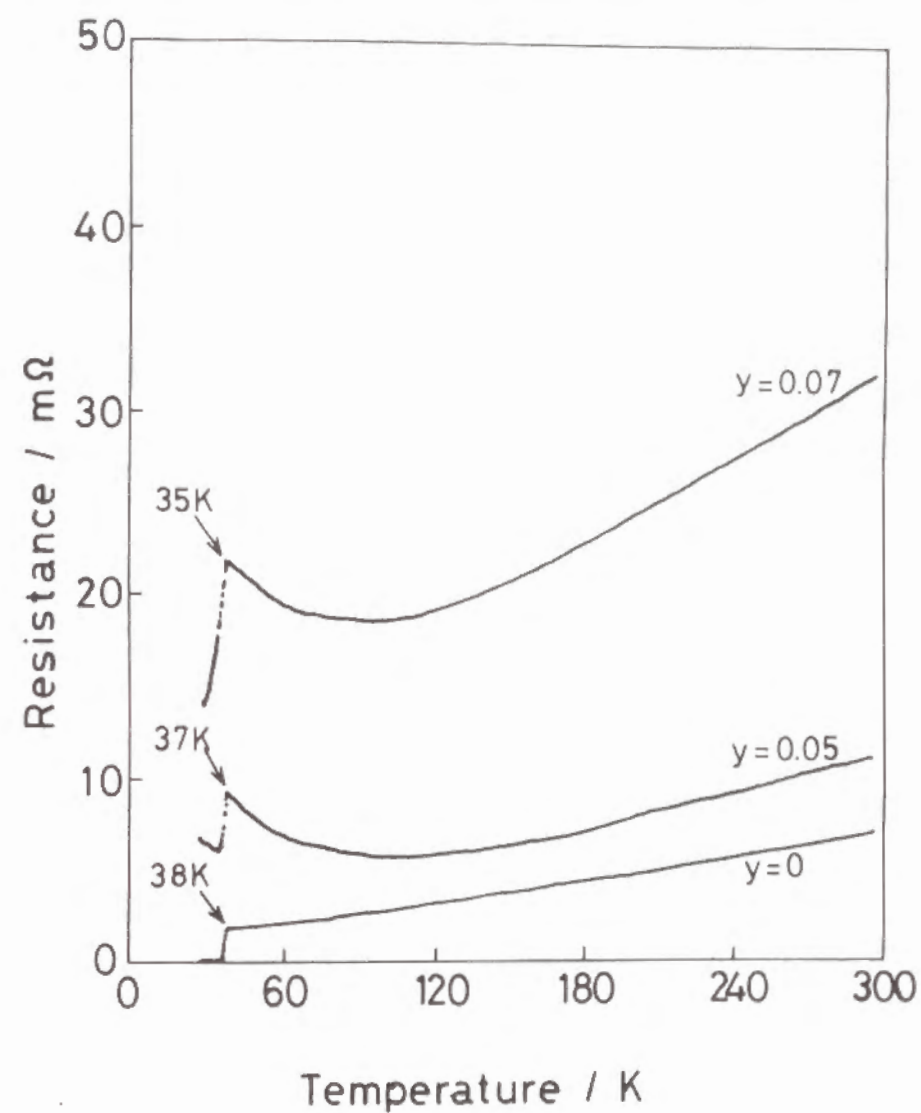


Fig. 6. (a) Temperature dependence of the electrical resistance of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ with $y=0, 0.05$ and 0.07 .

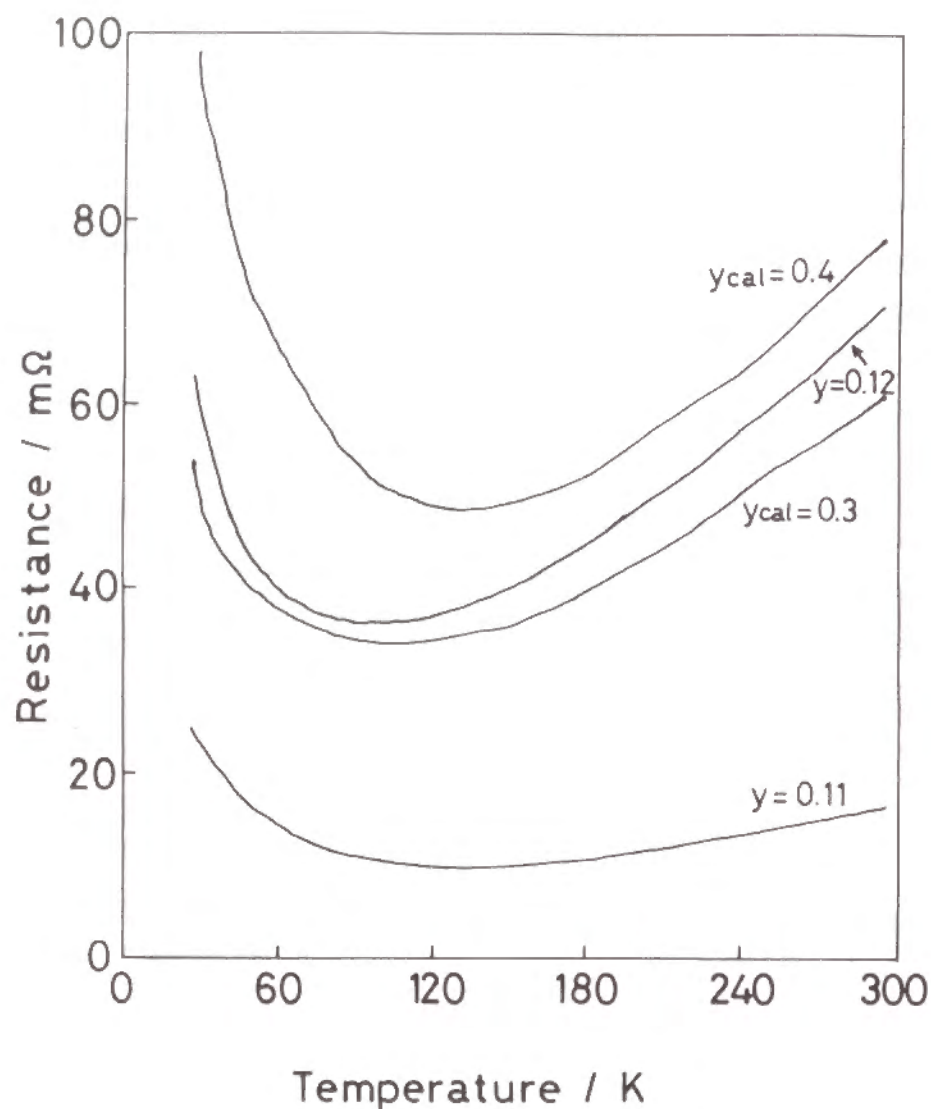


Fig. 6. (b) Temperature dependence of the electrical resistance of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ with $y=0.11$, 0.12 and $y_{\text{cal}}=0.3$ and 0.4 .

samples are summarized in Table III. $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$, which contains no sulfur, shows T_c (onset) at 38 K and T_c (end) at 36 K. Sulfur-doped samples with $y=0.05$ and 0.07 show 1 - 3 K lower superconducting transition temperatures than $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$. While $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ shows totally metallic behavior in the resistance-temperature curve, sulfur-doped samples show semiconducting behavior in the lower temperature region without giving the zero-resistance. T_c (onset) decreases and the resistance increases with increasing sulfur content. In the samples with higher sulfur content of $y \geq 0.11$, no superconducting transition was observed, at least above 28 K.

3.5. Magnetic Susceptibility

Figure 7 shows the temperature dependence of the a.c. magnetic susceptibility of the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ samples with $y=0$, 0.05 and 0.07 . The samples of $y=0$ and 0.05 show the large signal of diamagnetism at temperatures below 33 K ($=T_c(\chi)$), which clearly indicates the existence of a large amount of superconducting phase in the samples. On the other hand, the sample of $y=0.07$ does not show the superconductivity although the transition has been observed at 35 K in the resistance curve as shown in Fig. 6 (a).

4. DISCUSSION

4.1. Metal-Semiconductor Transition of the Sulfur-Doped Samples

All of the sulfur-doped samples $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ show the transition from metallic to semiconducting behavior with decreasing temperature, whereas $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ shows totally metallic conductivity above T_c as seen in Fig. 6. This phenomenon can be explained on the basis of the electronic structure of

Table III Superconducting transition temperature of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$.

y	T_c (onset) /K	T_c (end) /K	T_c (χ) /K
0	38	36	33
0.05	37	-	33
0.07	35	-	-

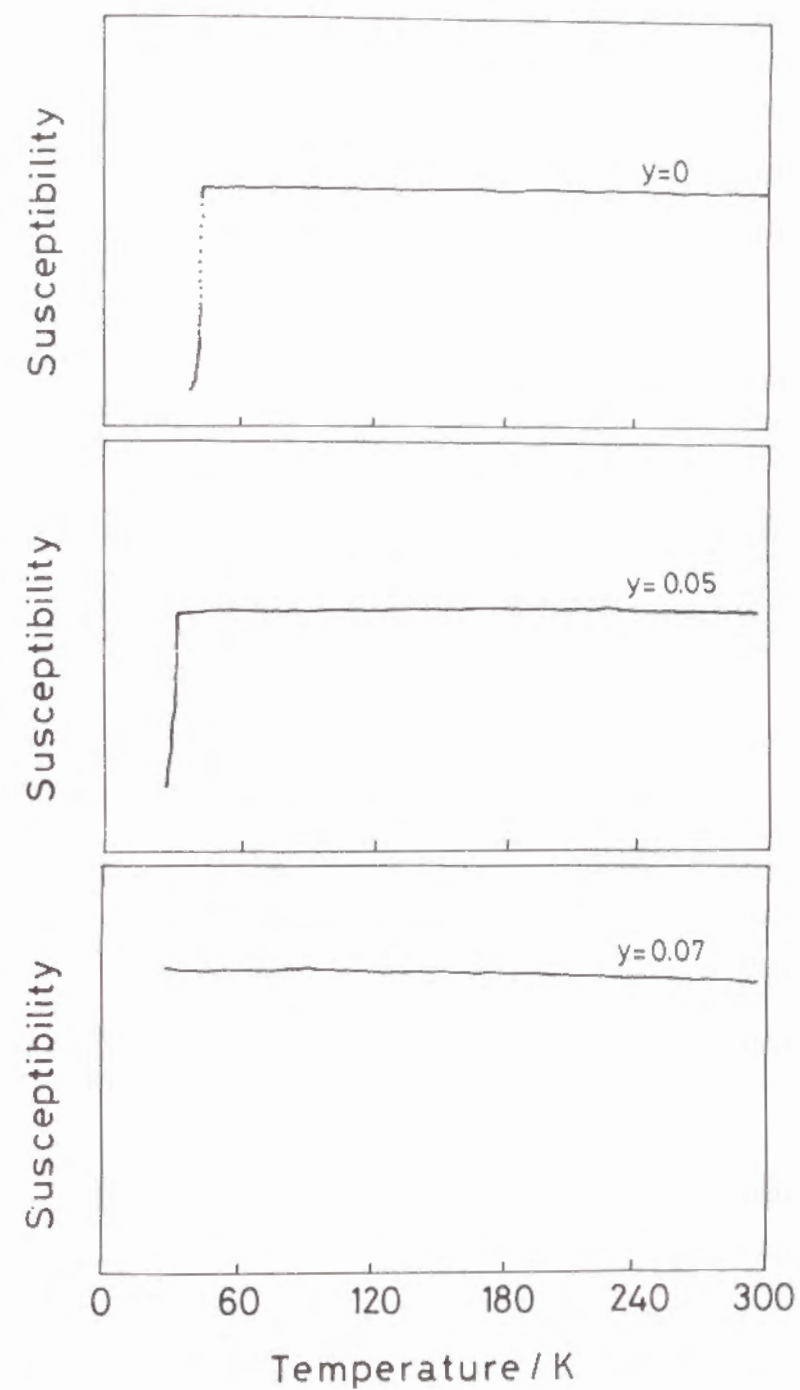


Fig. 7. Temperature dependence of the a.c. magnetic susceptibility of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ with $y=0, 0.05$ and 0.07 .

La_2CuO_4 [6] which is the parent material of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ solid solutions. Because the Cu^{2+} ions with $3d^9$ electronic configuration in La_2CuO_4 are octahedrally coordinated by six oxygens in the K_2NiF_4 -type structure as shown in Fig. 1, the $3d$ orbitals of Cu^{2+} are separated into five energy levels due to the Jahn-Teller effect. The highest energy level $\text{Cu-}3d_{x^2-y^2}$, which is directed to oxygens in the CuO_2 plane, is half-filled with an electron. Because of the strong Coulomb interaction between these electrons, the $\text{Cu-}3d_{x^2-y^2}$ band is split into two bands, the upper Hubbard band and the lower Hubbard band, forming the Hubbard gap between these two bands as shown in Fig. 8. The lower Hubbard band is filled and the upper is empty. The $\text{O-}2p$ band lies in the Hubbard gap, forming the energy gap with the upper Hubbard band, which is called the charge transfer (CT) gap. The $\text{O-}2p$ band and the upper Hubbard band of Cu form the hybrid band of the anti-bonding $\sigma^*_{x^2-y^2}$, which is not totally filled with electron. With decreasing temperature, the hybridization of these bands becomes smaller and finally disappears to form CT gap, showing the metal-semiconductor transition depending on temperature.

When the Sr^{2+} ions are substituted for La^{3+} in La_2CuO_4 , holes are doped in the CuO_2 plane for the charge compensation, resulting in the totally metallic conduction at any temperatures. In other words, the metal-semiconductor transition is suppressed with increasing hole concentration in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system. Therefore, the occurrence of the metal-semiconductor transition in the present sulfur-doped samples may result from the reducing hole concentration in the CuO_2 plane. Further discussion on this point will be given in Section 2.

4.2. Relation between Structure and Superconductivity

There are several discussions on the relationship between the appearance

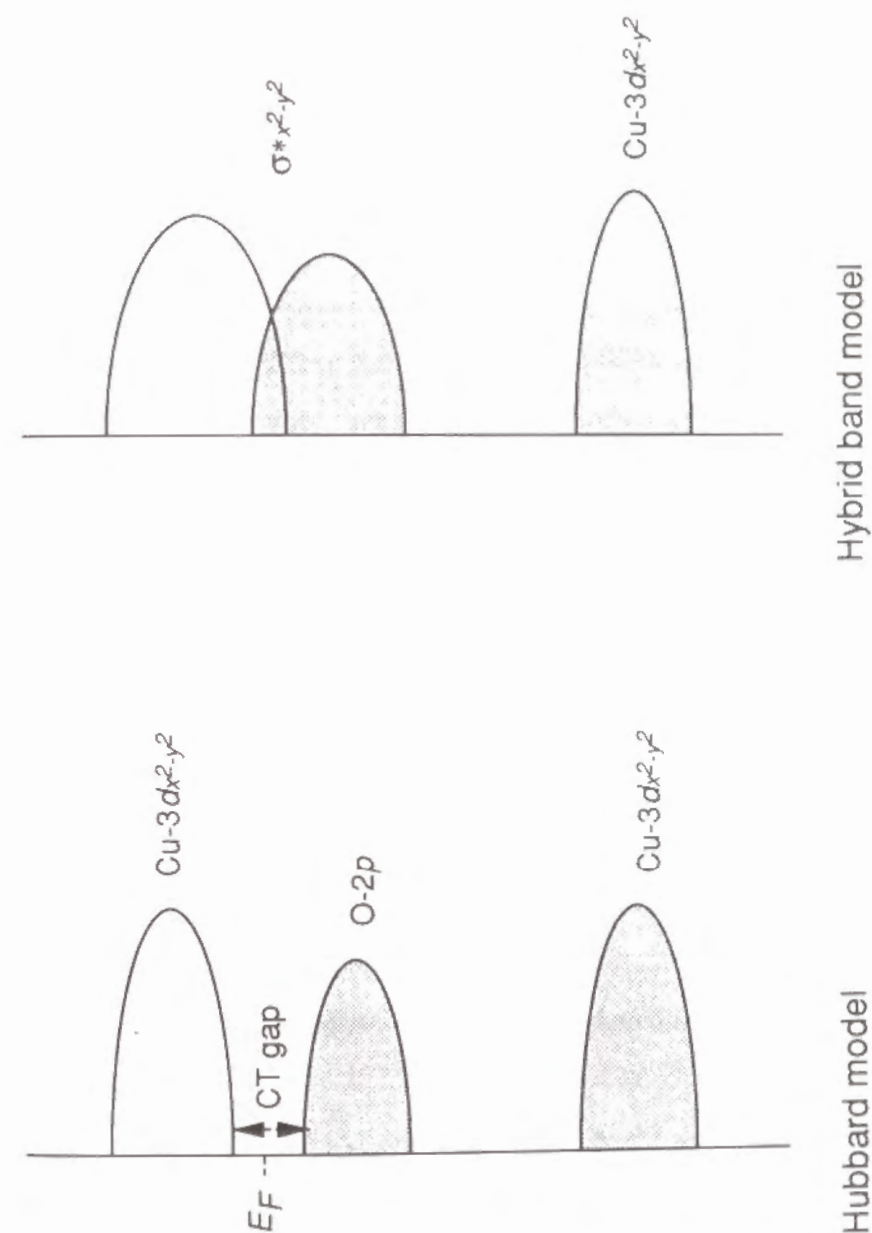


Fig. 8. Schematic model for the electronic structure of La_2CuO_4 . The hybrid band model is more suitable to explain the observed electrical properties.

of superconductivity and the tetragonal-to-orthorhombic phase transition. Fleming *et al.* [7] pointed out that in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, tetragonal-to-orthorhombic transition temperature T_s decreases from 533 K to zero when the amount of strontium x increases from 0 to 0.20, and the volume fraction of ideal diamagnetism increases with increasing strontium concentration, becoming maximum at the composition range where T_s is approaching the superconducting transition temperatures. Torrance *et al.* [1], however, concluded that the tetragonal-to-orthorhombic transition itself has no relation to superconductivity on the basis of the fact that the structural phase transition is observed only for $x \leq 0.19$, whereas superconductivity is observed until $x = 0.26$. It seems that a critical conclusion on the relation between the phase transition and superconductivity cannot be provided at present.

Apparent compositional changes similar to those taking place in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system can be noticed in the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ system. The noticeable changes caused by incorporation of sulfur into $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ are the change in the crystal structure at room temperature from tetragonal to orthorhombic and the degradation of superconductivity. The change in crystal structure at room temperature from tetragonal to orthorhombic implies an increase in the tetragonal-to-orthorhombic phase transition temperature T_s with increasing sulfur content. Such a relation between the increase in T_s and the decrease in T_c is also observed in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system with decreasing strontium concentration from $x = 0.16$ to 0.

Elongation along the in-plane axes and shrinkage along the c -axis, which are observed in the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ system with increasing sulfur content, are also observed in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system with decreasing strontium content from $x = 0.16$ to 0. In both cases, the degradation of superconductivity is

accompanied by such changes of the lattice constants. Fleming *et al.* [7] considered decreases in the in-plane lattice constants a and b and an increase in the lattice constant c , that is, the increasing distortion of CuO_6 octahedra in the crystal structure, as an increase in two-dimensionality of the structure which is important for the occurrence of superconductivity. In the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ system, change of the lattice constants with increasing sulfur content results in the less two-dimensional structure corresponding to less distorted CuO_6 octahedra. In other words, the axial oxygens come closer to the CuO_2 plane, increasing the electronic interaction between the axial oxygens and copper atoms, which may cause the suppression of superconductivity.

On the basis of the fact that the substitution of sulfur for oxygen in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ leads to elongation of the in-plane axes and shrinkage of the c -axis, sulfur ions are considered to be incorporated in the in-plane sites of the CuO_2 plane because S^{2-} ion (0.184 nm) is larger than O^{2-} ion (0.138 nm) [8]. Considering the fact that the covalency of the Cu-S bond is larger than that of the Cu-O bond [3], the electronic density of Cu in the region along the Cu-S bond is higher than that of oxygen-bonded Cu. This indicates that the formal charge of Cu in the sulfur-doped samples may be lower than that of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$. Since the hole concentration of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$, which has almost no oxygen vacancies, is determined by the Sr concentration and for $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$ the sulfur-substituted oxygens are less than 3 %, it can be said that the change of the total hole concentration is less important factor affecting the degradation of superconductivity in this case.

5. CONCLUSION

The replacement of oxygen by sulfur was attempted in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$

superconductor, and the following changes in the crystal structure and electrical properties were found. Superconductivity was degraded as the sulfur concentration increased in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$; superconducting transition temperature T_c decreased, semiconducting behavior in the temperature dependence of electrical resistance at low temperatures appeared and the electrical resistance increased with increasing sulfur concentration. The crystal structure at room temperature changed from tetragonal to orthorhombic, the in-plane lattice constants increased and the c -axis shrank with increasing sulfur content. These features of changes in the crystal structure and electrical properties seemed to be similar to those observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system with strontium content decreasing from $x=0.16$ to zero.

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SECTION 2 EFFECTS OF SULFUR SUBSTITUTION ON NON-SUPERCONDUCTING $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ AND $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_4$

1. INTRODUCTION

It has been reported that the electrical properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ vary with the Sr concentration x from Mott insulator for $0 \leq x \leq 0.06$ to superconductor for $0.06 \leq x \leq 0.26$ to normal metal for $0.26 \leq x$ [1]. In Section 1, it has been shown that in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$, which shows the highest superconducting transition temperature T_c in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, the sulfur substitution for oxygen leads to the changes in the crystal structure and electrical properties; that is, the in-plane lattice constants increase and the lattice constant c decreases monotonically and the superconducting transition temperature decreases with increasing sulfur content [2]. It has not been clear yet, however, which is responsible for T_c , structure or hole concentration. In this section, in order to understand what governs T_c on sulfur substitution, effects of the sulfur substitution on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with higher strontium concentration, namely $x=0.26$ and 0.30 at which superconductivity disappears and metallic behavior is observed, have been investigated.

2. EXPERIMENTAL

2.1. Sample Preparation

Samples of the nominal composition of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$, where $x=0.26$,

0.30 and $y=0, 0.10, 0.20$, were prepared from high-purity reagent grade La_2O_3 , SrCO_3 , CuO and CuS by the solid-state reaction. The chemicals were mixed and calcined by heating at 900°C for 5 or 10 h in air. A heating rate of $5^\circ\text{C}/\text{min}$ was adopted. The calcined powder was ground and pressed into pellets of 20 mm diameter and 1-1.5 mm thick. The pellets were sintered at 1000°C or 1100°C for 10 h in air and cooled slowly in the furnace to room temperature.

2.2. X-Ray Analysis

The x-ray diffraction (XRD) pattern of the samples were taken for the identification of the crystalline phases with a Rigaku Denki Company model RAD-IIA using $\text{CuK}\alpha$ radiation. The lattice constants of the crystal were determined for the samples of $x=0.26$ by the internal standard method using Si as the internal standard substance. The sulfur content in the samples was determined by the x-ray fluorescence analysis with a Rigaku Denki Company model KG-4 x-ray fluorescence analyzer.

2.3. Measurement of Superconductivity

The d.c. electrical resistance of the samples was measured at temperatures from 300 K to 28 K by the four-probe method. The a.c. magnetic susceptibility of the samples was measured from 300 K to 28 K by the Hartshorn bridge method with a frequency of 270 Hz and an amplitude of 100 mV. The d.c. magnetic susceptibility of several samples was measured from 50 K to 5 K with a Quantum Design MPMS SQUID magnetometer in a static magnetic field of 20 Oe.

3. RESULTS

3.1. Sulfur Content

The analyzed sulfur content y of all the samples are plotted against the calculated sulfur content of the starting composition in Fig. 1. It is shown that more than 70 % of sulfur in the starting mixture remains in the sintered products. In order to prepare $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ with high Sr concentration, the heat treatment in oxygen is more suitable than that in air. Nevertheless, in this work the heat treatment had to be conducted in air; otherwise sulfur may be oxidized and may not remain in the solid solution as S^{2-} . In the following, y represents the analyzed sulfur content.

3.2. Phase Analysis

The sintering conditions, the analyzed sulfur content and the crystalline phases in the products are summarized in Table I. Figure 2 shows the XRD patterns of the sintered pellets. For $x=0.26$, all the samples, whose y values are 0, 0.10 and 0.16, are obtained as the single phase of the K_2NiF_4 -type structure by heating at 1000 °C for 10 h. For $x=0.30$, the single-phase sample is obtained for $y=0.09$ and 0.14 but can not be obtained for $y=0$ by heating at 1000 °C for 10 h. The sample of $x=0.30$ and $y=0$ without sulfur substitution does not provide the single phase by heating at 1100 °C for 10 h. Under this heating condition, sulfur-containing samples of $x=0.30$ and $y=0.07$ and 0.19 are also obtained as the single phase. All the single-phase samples have a tetragonal K_2NiF_4 -type structure at room temperature.

3.3. Lattice Constants

The values of the lattice constants a and c of the $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$

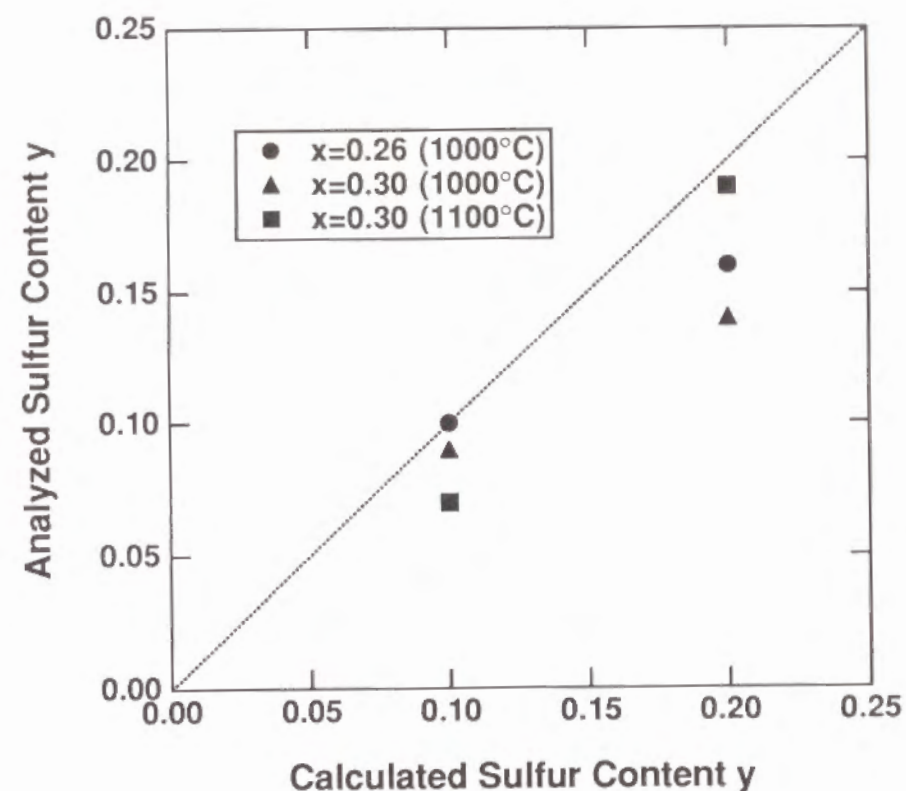


Fig. 1. Relation between the analyzed sulfur content and the calculated sulfur content in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$.

Table I The sintering condition, the analyzed sulfur content, y , and the crystalline phases in the products of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$.

Sample No.	x	y_{cal}	Sintering Condition	y	Crystalline Phases
1	0.26	0	1000°C, 10h, air	0	K_2NiF_4 -type
2	0.26	0.10	1000°C, 10h, air	0.10	K_2NiF_4 -type
3	0.26	0.20	1000°C, 10h, air	0.16	K_2NiF_4 -type
4	0.30	0	1000°C, 10h, air	0	K_2NiF_4 -type, $\text{La}_2\text{SrCu}_2\text{O}_6$
5	0.30	0.10	1000°C, 10h, air	0.09	K_2NiF_4 -type
6	0.30	0.20	1000°C, 10h, air	0.14	K_2NiF_4 -type
7	0.30	0	1100°C, 10h, air	0	K_2NiF_4 -type
8	0.30	0.10	1100°C, 10h, air	0.07	K_2NiF_4 -type
9	0.30	0.20	1100°C, 10h, air	0.19	K_2NiF_4 -type

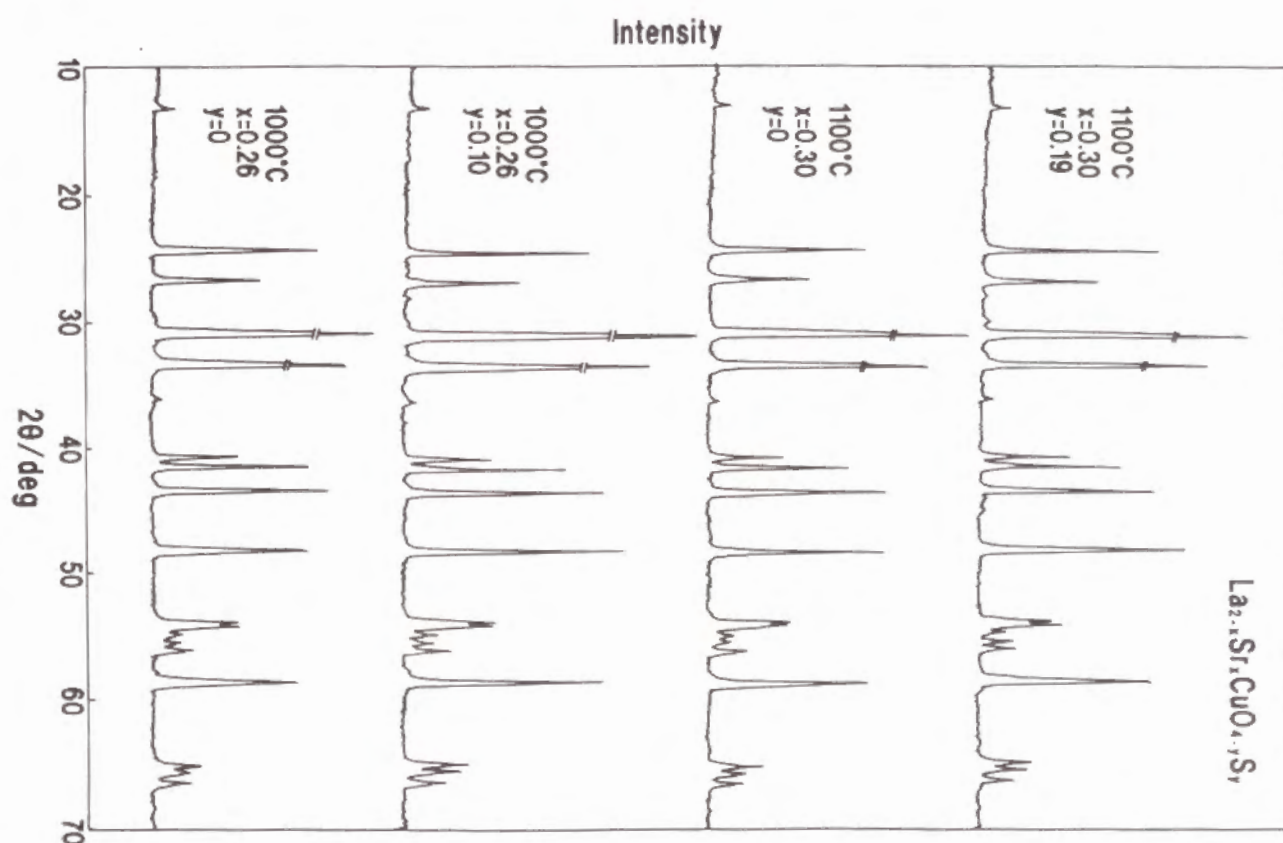


Fig. 2. The XRD patterns of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ samples with $(x, y) = (0.26, 0)$, $(0.26, 0.10)$, $(0.30, 0)$ and $(0.30, 0.19)$.

samples are given in Table II. Any significant change in the lattice constants is not observed with varying sulfur content y . The a -axis value is smaller and the c -axis value is larger than those of $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ [2], which has the highest T_c of 40 K.

3.4. Superconducting Properties

The temperature dependence of the d.c. electrical resistance of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ is shown in Fig. 3. The sample with no sulfur, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$, shows metallic conduction and superconducting transition at 37 K. The sulfur-containing sample of $y=0.10$, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.90}\text{S}_{0.10}$, also shows metallic conduction and T_c (onset) at 39 K and T_c (end) at 35 K. The sample of $y=0.16$, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.84}\text{S}_{0.16}$, shows semiconducting behavior in the lower temperature range and T_c (onset) at 38 K, but zero-resistance is not observed at least above 28 K. Figure 4 shows the temperature-resistance curve of $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{4-y}\text{S}_y$. It is seen that all three samples with $y=0, 0.09$ and 0.14 show metallic conduction at higher temperatures and superconducting transition at 38 K.

Figure 5 shows the temperature dependence of the a.c. magnetic susceptibility of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ samples. Four samples with $(x, y)=(0.26, 0.10)$, $(0.26, 0.16)$, $(0.30, 0.14)$ and $(0.30, 0.19)$ show the signal of diamagnetism above 28 K. The other samples do not show superconducting transition.

The temperature dependence of the d.c. magnetic susceptibility of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ measured by SQUID is shown in Fig. 6. The Meissner volume fraction of the sulfur-substituted sample of $y=0.10$ at 5 K is much larger than that of the sample containing no sulfur. This result indicates that the sample with no sulfur, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$, contains a relatively small amount of superconducting phase, while the sulfur-substituted sample contains a larger

Table II Lattice constants a and c of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$.

Sulfur Content y	Lattice Constants / nm	
	a	c
0	0.377	1.324
0.10	0.377	1.324
0.16	0.378	1.322

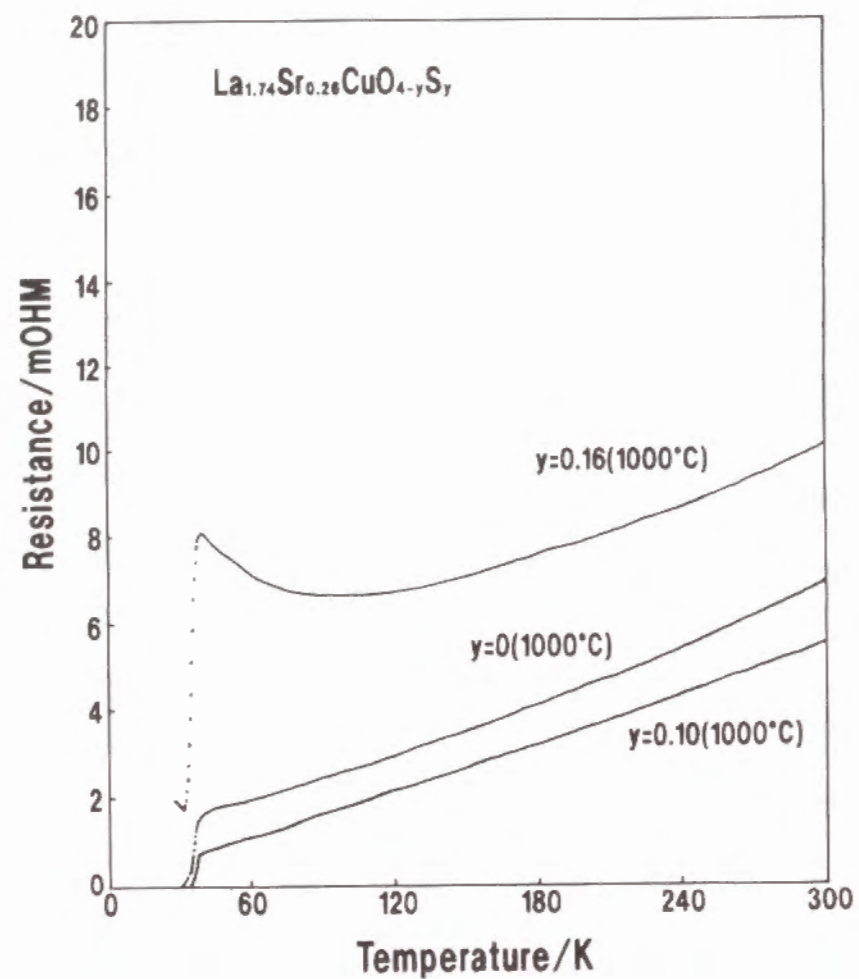


Fig. 3. Temperature dependence of the electrical resistance of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ with $y=0, 0.10$ and 0.16 sintered at 1000°C .

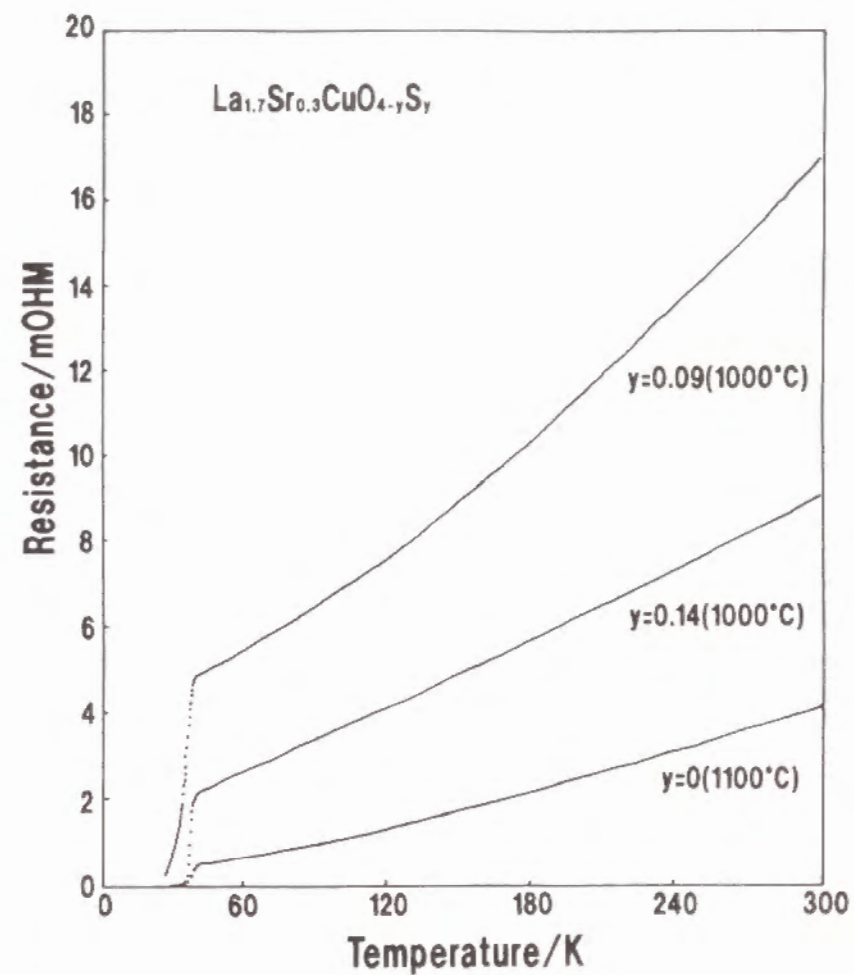


Fig. 4. Temperature dependence of the electrical resistance of $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{4-y}\text{S}_y$ with $y=0, 0.09$ and 0.14 sintered at 1000 or 1100°C .

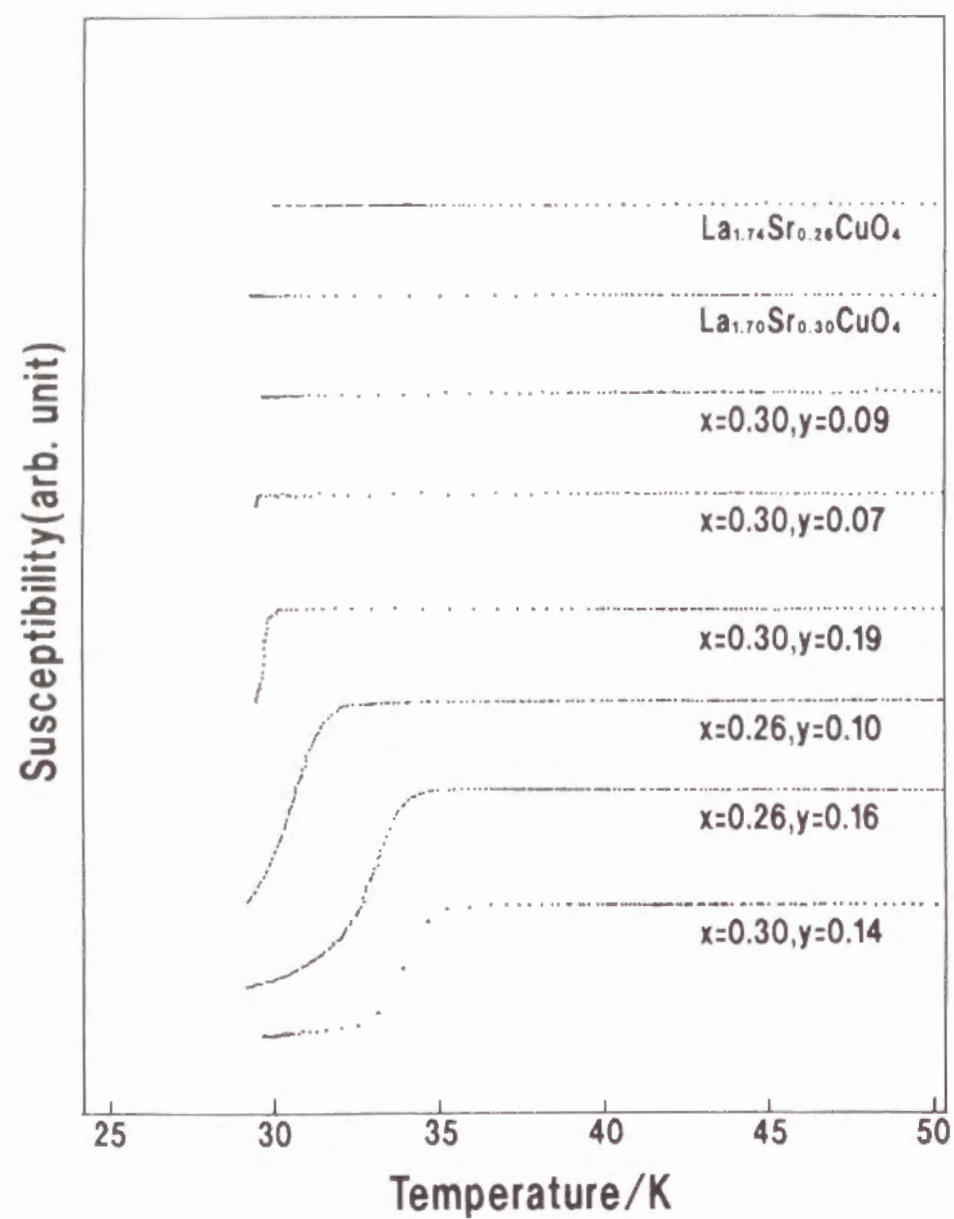


Fig. 5. Temperature dependence of the a.c. magnetic susceptibility of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ samples.

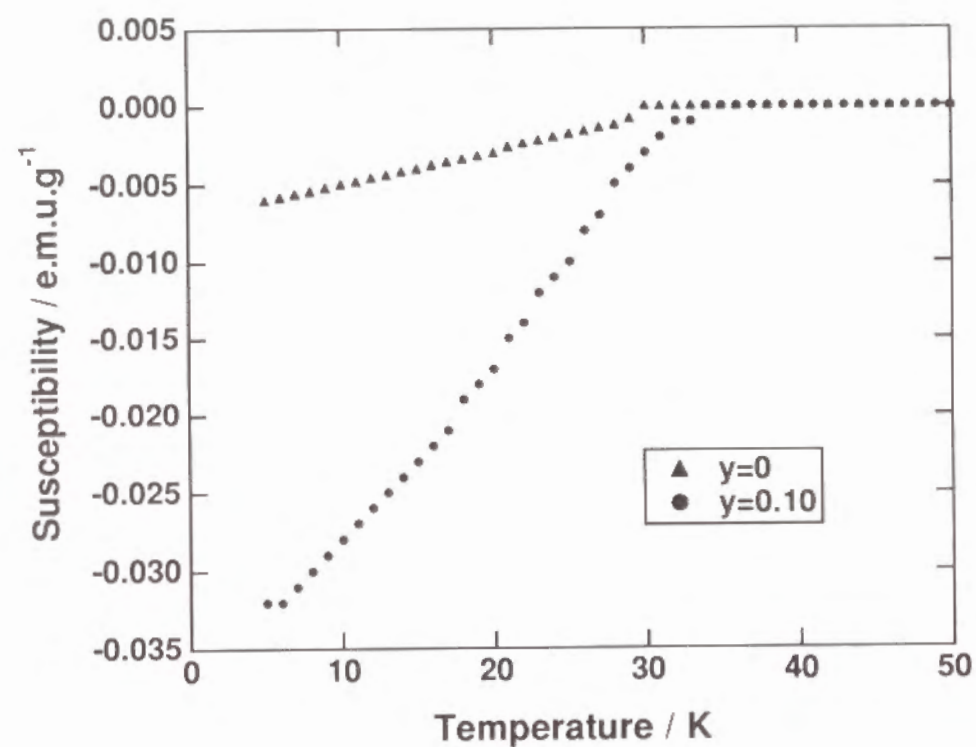


Fig. 6. Temperature dependence of the d.c. magnetic susceptibility of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$.

amount of superconducting phase. The larger Meissner volume fraction of the latter sample is considered to result from the substitution of sulfur for oxygen, as discussed below.

The composition and superconducting transition temperature of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ are summarized in Table III. All the samples show T_c (onset) at temperatures between 37 K and 39 K according to the resistance data, whereas only the sulfur-doped samples show superconducting transition above 30 K according to the a.c. magnetic susceptibility data. Figure 7 shows the range of the Sr concentration x and the sulfur concentration y in which the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions exhibit the superconducting transition above 30 K in susceptibility. It is seen that the superconducting range shifts to the higher Sr concentration region with increasing sulfur content y .

4. DISCUSSION

4.1. Presence of Superconductivity in the Nominal Composition

$\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ in the Resistance Measurement

It has been reported by Torrance *et al.* [1] that the superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ disappears at the Sr content x equaling 0.26. In the present work, however, $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ composition corresponding to $x=0.26$ has shown the superconducting transition at 38 K according to the resistance data. This discrepancy may be assumed to arise from the difference in the heating atmosphere in the preparation process and the resulting absence or presence of oxygen vacancies in the products. The distribution of oxygen vacancies, furthermore, is considered to result in the phase inhomogeneity of the sample. The inhomogeneous phases are theoretically discriminated by the different oxygen

Table III Composition and superconducting transition temperature of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$.

x	y	T_c (onset) /K	T_c (end) /K	T_c (χ) /K
0.26	0	37	32	-
0.26	0.10	39	35	32
0.26	0.16	38	-	34
0.30	0	38	34	-
0.30	0.07	37	-	-
0.30	0.09	38	-	-
0.30	0.14	38	35	35
0.30	0.19	37	-	30

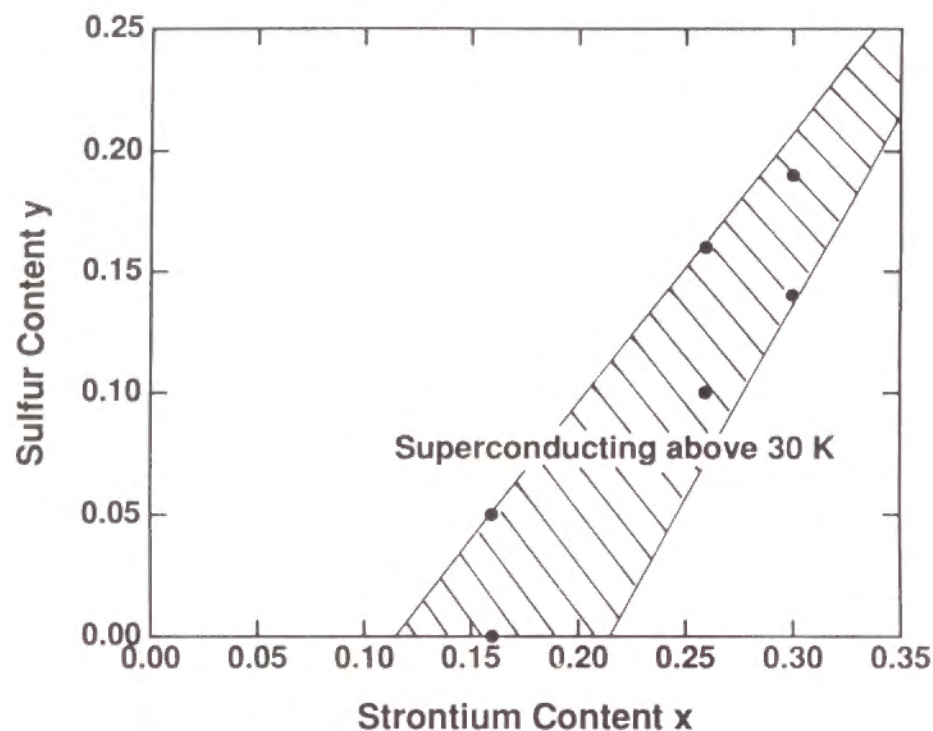


Fig. 7. Relation between the strontium content x and the sulfur content y in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ which shows superconducting transition above 30 K on the measurement of the susceptibility.

content [1]. It is plausible to assume that the product of Torrance *et al.* has an exact composition of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ as to the oxygen content and accordingly has no oxygen vacancies because their product was produced in pure oxygen gas, whereas in the present product some oxygens should be lost, leaving some oxygen vacancies behind and then causing the phase inhomogeneity, because the firing was made in air.

The formation of oxygen vacancies may correspond to a decrease in the hole concentration. According to Shafer *et al.* [3] and Torrance *et al.* [1], the occurrence of superconductivity in the range of $0.06 \leq x \leq 0.26$ in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system is attributed to the presence of suitable concentrations of holes and the disappearance of superconductivity at $x=0.26$ for their products may be caused by the presence of excessive holes. In other words, there are upper and lower limits of hole concentration in the CuO_2 plane for the occurrence of superconductivity in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compositions. Then, it can be assumed that in the present work, heating the composition of $x=0.26$ in air causes the formation of oxygen vacancies and the phase inhomogeneity, and the appearance of the phase that has lower hole concentration than the upper limit results in the occurrence of superconductivity. The susceptibility curve of the present $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_4$ composition denoted $y=0$ in Fig. 6 shows that a small amount of diamagnetism starts to appear below around the T_c (onset) found by the resistance-temperature curve, indicating the presence of a small amount of superconducting phase.

4.2. The Effects of Sulfur Doping on the Superconductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$

The effects of the sulfur content, y , in $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ compositions on their superconductivity will be discussed by referring to the effect of the Sr

content, x , in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compositions on their superconducting behavior.

According to Torrance *et al.* [1], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ compositions are superconducting in the composition range $0.06 \leq x \leq 0.26$, and the lattice constant a decreases and the lattice constant c increases with increasing Sr content x until about $x=0.28$. Above $x=0.28$, the lattice constant a increases and c decreases with increasing x . The latter change in the lattice constants corresponds to an increase in oxygen vacancies. The present sample of composition $x=0.26$ showing superconductivity prepared in air of lower oxygen partial pressure than pure oxygen has a larger a value and a smaller c value than the sample of $x=0.26$ prepared by Torrance *et al.* [1], which imply that the present sample has a higher amount of oxygen vacancies.

According to the results in Section 1, the lattice constant a increases and the c decreases with increasing sulfur content y in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ at the composition of $x=0.16$, which might have few oxygen vacancies. On the contrary, as shown in Table II, the composition of $y=0.10$ in the formula $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ has the same a and c values as those of the composition of $y=0$, which contains no sulfur. It is probable that the replacement of oxygen by sulfur suppresses the formation of oxygen vacancies; otherwise the lattice constant a would increase and the c would decrease due to the increase in sulfur content.

On the other hand, the susceptibility measurement shown in Fig. 6 indicates that the addition of sulfur in an amount corresponding to $y=0.10$ increases the degree of diamagnetism below T_c and, accordingly, the amount of the superconducting phase. This is in contrary to what is expected from the simple concept that the decrease in the amount of oxygen vacancies is accompanied by the increase in the hole concentration in the CuO_2 plane, which may exceed the

upper limit to the superconductivity at the composition of $x=0.26$. Therefore, the explanation is proposed that the incorporation of sulfur may change the electronic structure of the CuO_2 plane so that the concentration of holes related to superconductivity (delocalized holes) might be decreased.

The effect of S is explained on the basis of the difference in electronegativity between oxygen and sulfur. Copper atoms neighboring sulfur atoms have a larger electronic density than other copper atoms coordinated by only oxygens, because the electronegativity of sulfur is lower than that of oxygen. It is expected then that a part of holes may be trapped and localized by the higher electronic density region centered around sulfur atoms, changing into non-effective, localized holes. This would reduce the concentration of superconductivity-related holes, in other words, sulfur doping effectively lowers the hole concentration in the CuO_2 plane.

Based on the above discussion, a concept is proposed that in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions, the electrical and magnetic properties related to superconductivity may be determined by " $x-y$ ", that is, the difference of Sr content x and S content y . The system loses superconductivity when " $x-y$ " is too large (x is large and S content is small) or too small (S content is too large). The application of this assumption to the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}\text{S}_y$ compositions having $x=0.26$ and $x=0.30$ explain the presence or absence of superconductivity of the compositions as follows. The too large " $x-y$ " values of $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.93}\text{S}_{0.07}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.91}\text{S}_{0.09}$ imply the insufficient suppression of the hole concentration to reach the upper limit for the appearance of superconductivity. The small " $x-y$ " values of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.84}\text{S}_{0.16}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.81}\text{S}_{0.19}$ lead to the excessive lowering of the hole concentration resulting in their semiconducting behavior in the lower temperature region. The compositions

$\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{3.90}\text{S}_{0.10}$ and $\text{La}_{1.70}\text{Sr}_{0.30}\text{CuO}_{3.84}\text{S}_{0.16}$ have moderate hole concentrations at which superconducting transition at 30 - 40 K is observed in both the resistance and the susceptibility measurement, as shown in Table III.

5. CONCLUSION

The effects of sulfur substitution on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.26, 0.30$) were studied. It was considered that the sulfur substitution reduces the excessive hole concentration of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at higher Sr concentration. The lattice constants of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ were almost constant in the range from $y=0$ to $y=0.16$, which indicates that sulfur substitution causes the change in electronic state rather than in structure. The sulfur substituted samples exhibited superconducting transition at 37-39 K and the larger Meissner volume fraction than the samples with no sulfur. It was found that the region in which $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shows superconductivity shifts to higher Sr concentrations with increasing sulfur content y .

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CHAPTER 5

SYNTHESIS, STRUCTURE AND PROPERTIES OF $\text{La}_{1-x}\text{M}_x\text{SrFeO}_4$ (M=Ca, Sr, Ba, Y)

1. INTRODUCTION

Since the discovery of high-temperature superconductivity in a series of copper oxide systems [1-3], perovskite-related 3d transition metal oxides have attracted renewed attention in understanding the mechanism of superconductivity and in searching for new superconductors. From this standpoint, the perovskite-type NdNiO_{3-y} has been investigated in Chapter. 3. Likewise, A_2BO_4 compounds (A = rare earth and/or alkaline earth and B = transition metal) with K_2NiF_4 structure have been the targets of intensive studies because of their structural similarity to the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ superconductor.

It is well-known [4-6] that the properties of A_2BO_4 compounds change depending on the formal valence of transition metal ions and/or the lattice constants. The valence of B ions in A_2BO_4 is variable with ionic substitution at A-site or varying oxygen contents. For example, an increase in Sr^{2+} ions substituted for La^{3+} in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ results in change in the formal valence of copper from Cu^{2+} for $x=0$ to Cu^{2+} and Cu^{3+} mixed state for $0 < x < 1$, and the

electrical conducting behavior changes with x from insulating for $0 \leq x \leq 0.06$ to superconducting for $0.06 \leq x \leq 0.26$ to metallic for $0.26 \leq x$ [4]. In $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ [5], the mixed valence state can be attained, where the $\text{Ni}^{2+}/\text{Ni}^{3+}$ state results in semiconduction while the $\text{Ni}^{3+}/\text{Ni}^{4+}$ state results in metallic conductivity.

The change in the formal valence of transition metal ions is often followed by the change in the lattice constants; that is, the change in the oxidation state of transition metal ions gives rise to change in interaction between the transition metal ions and oxygen ions, which in turn makes the lattice constants change. It is known that the lattice constant a decreases and c increases with increasing x in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, since $\text{Cu}^{3+}-\text{O}^{2-}$ bonds are stronger than $\text{Cu}^{2+}-\text{O}^{2-}$ bonds in the CuO_2 planes. The change in the lattice constants without any changes in the formal valence also affects the properties of A_2BO_4 . Superconducting $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and $\text{La}_{2-x}\text{Ca}_x\text{CuO}_4$ of the same x values exhibit different superconducting transition temperatures [4,6,7], which results from their different lattice constants due to different ionic radii of alkaline earths.

A series of $(\text{La}, \text{Sr})_2\text{FeO}_4$ solid solutions with K_2NiF_4 structure (see Fig.1) show different electrical properties depending on the valence of iron and/or the La:Sr ratio. It was reported by King *et al.* [8] that at room temperature La_2FeO_4 with Fe^{2+} is insulating with resistivity of $>10^7 \Omega\text{-cm}$, and $\text{La}_{1.5}\text{Sr}_{0.5}\text{FeO}_4$ with mixed $\text{Fe}^{2+}/\text{Fe}^{3+}$ and LaSrFeO_4 with Fe^{3+} are semiconducting with resistivity of $9.8 \times 10^3 \Omega\text{-cm}$ and $2.4 \times 10^3 \Omega\text{-cm}$, respectively. Although the exact valence of iron was not determined in their work, at least it seems that the resistivity of $(\text{La}, \text{Sr})_2\text{FeO}_4$ decreases with increasing the ratio of the higher oxidation state of iron in the La-rich compositions.

It is interesting, therefore, to know whether the further oxidized state of iron or $\text{Fe}^{3+}/\text{Fe}^{4+}$ mixed state can be achieved and whether a decrease in resistivity

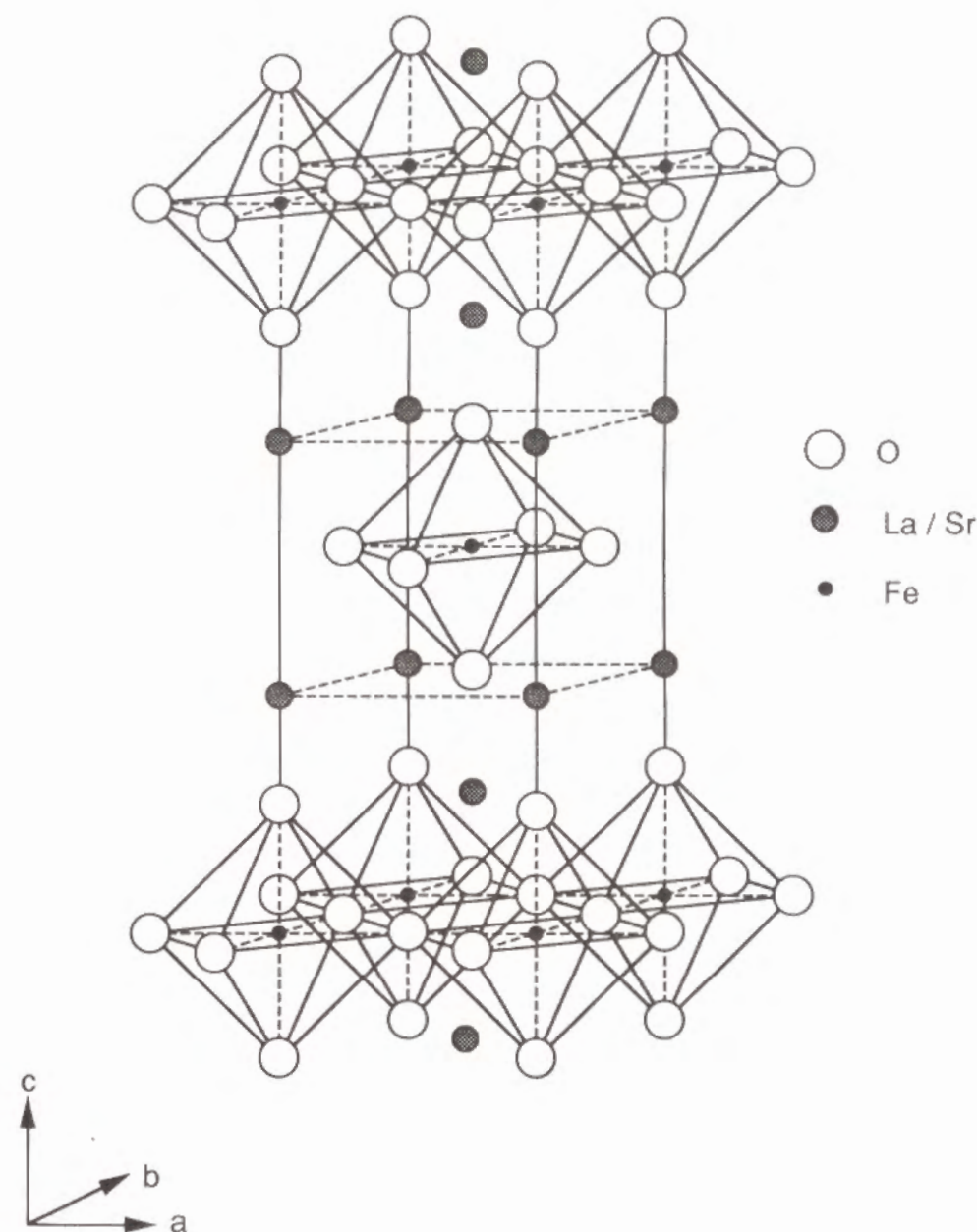


Fig. 1. The structure of LaSrFeO_4 .

to metallic state is observed in the $(\text{La}, \text{Sr})_2\text{FeO}_4$ system. No work has been reported so far, however, on the synthesis and properties of Sr-rich $(\text{La}, \text{Sr})_2\text{FeO}_4$ with $\text{Fe}^{3+}/\text{Fe}^{4+}$ mixed state. Moreover, if it is possible to substitute the other alkaline earth metals such as Ca or Ba for La in LaSrFeO_4 , it can be expected that the changes in both of the valence of iron and the lattice constants take place, which may result in the change in the electrical properties. The substitution of Y for La can be also expected to change the lattice constants without any change in the valence of Fe ions.

In this chapter, the effects of the substitution of alkaline earths (Ca, Sr and Ba) or Y for La on the structure and electrical properties of LaSrFeO_4 are examined. Using polycrystalline samples of $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$, $0 \leq x \leq 0.20$) and $\text{La}_{1-(x+y)}\text{Y}_y\text{Sr}_{1+x}\text{FeO}_4$ ($x=0.10$, $0 \leq y \leq 0.30$) prepared by the solid-state reaction, changes in the $\text{Fe}^{3+}/\text{Fe}^{4+}$ ratio, the lattice constants and the electrical properties with composition x and y and/or variation of substituents are investigated.

2. EXPERIMENTAL

2.1. Sample Preparation

$\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}$ and Ba) and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ were prepared by the solid-state reaction. The oxide and carbonate powder reagents, La_2O_3 (99.99%, Wako Pure Chemical Industries, Osaka, Japan), Y_2O_3 (99.99%, Wako Pure Chemical Industries), SrCO_3 (99.5%, Nacalai Tesque, Kyoto, Japan), CaCO_3 (99.5%, Nacalai Tesque), BaCO_3 (99.5%, Nacalai Tesque) and Fe_2O_3 (98.0%, Wako Pure Chemical Industries) were used as starting materials. The mixtures of the chemicals with desired atomic ratios were first

calcined at 1000 °C for 20 h in air. The calcined powders were ground and pressed into pellets of 13 mm diameter and about 1 mm thick under a pressure of 60 MPa, heated at 1400 °C for 20 h in air, and cooled in the furnace to room temperature. The resultant pellets were annealed in flowing oxygen at 700 °C for 50 h. In order to avoid contamination from the supports during the heat-treatment, the pellets were placed on the calcined powders of the same composition, which was supported on a platinum plate.

2.2. X-Ray Diffraction

The crystalline phases evolved in the samples after the heat-treatment were identified by the powder x-ray diffraction method (XRD) with a Rigaku Denki Company model RAD-IIA diffractometer using $\text{CuK}\alpha$ radiation. The lattice constants of the $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}$ and Ba) and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ crystals were determined by the XRD using Si as an internal standard substance.

2.3. EDTA Titration

The formal valence of Fe in the single-phase $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ was determined by the EDTA titration [9]. Figure 2 shows the schematic diagram of the titration. The pulverized sample (approximately 750 mg) was exactly weighed and dissolved in a 25 ml aqueous solution containing 1.5 ml of conc. HCl and 283.7 mg of FeCl_2 (corresponding to 125 mg of Fe^{2+}) at 60 °C while the solution was purged with CO_2 gas. Then the solution was cooled and diluted with CO_2 -saturated water to 50 ml, 1 ml of which was added to a buffer solution consisting of 1 N HCl and 1 M CH_3COONa with a volume ratio of 1:1. After adding a few drops of 1 % methanol solution of salicylic acid as indicator, the solution was titrated with 0.01 M EDTA standard solution to determine Fe^{3+} ions. Subsequently,

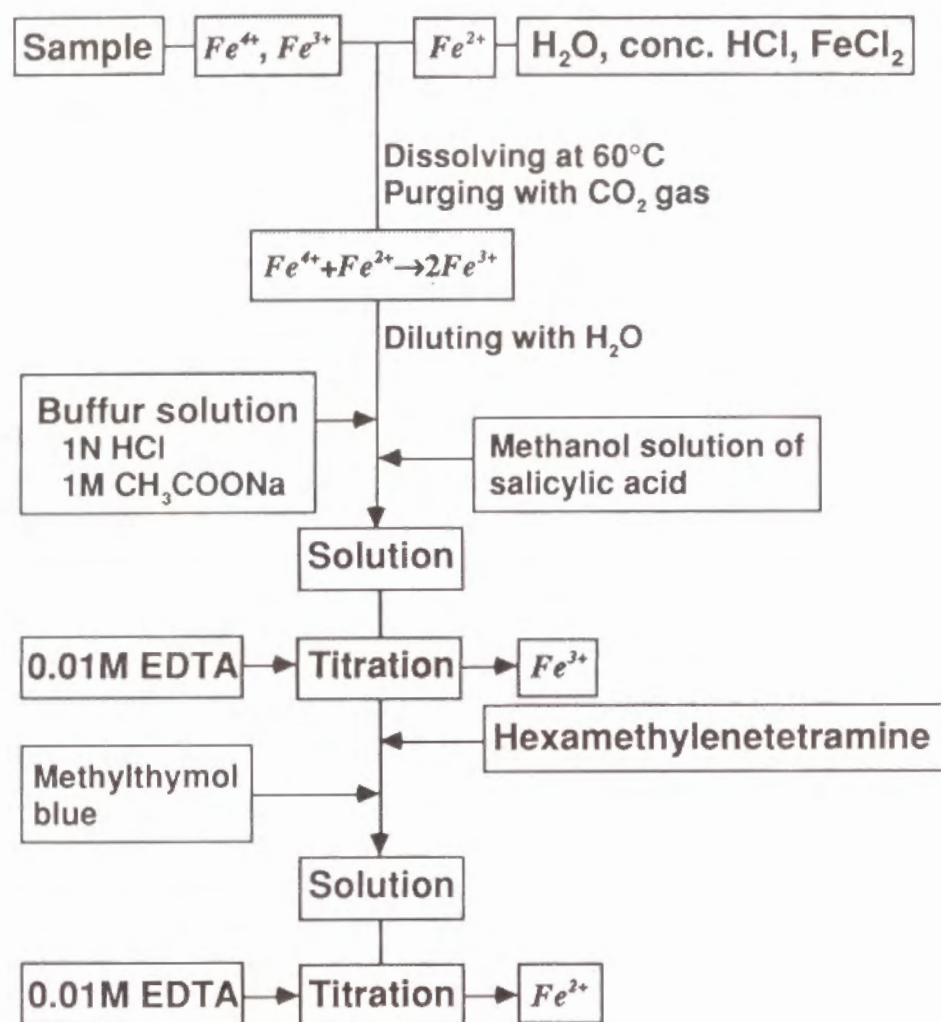


Fig. 2. The schematic diagram of the EDTA titration for the determination of the amount of Fe^{3+} and Fe^{4+} in the sample.

after adjusting the pH of the solution to 5 with an aqueous solution of hexamethylenetetramine and adding a 0.5 % aqueous solution of methylthymol blue as indicator, the resultant solution was placed in a water bath at $60^\circ C$ and titrated with 0.01 M EDTA standard solution to determine Fe^{2+} ions. Representing the amount of the first added Fe^{2+} by p and the determined Fe^{3+} and Fe^{2+} by q and r , respectively, the amount of Fe^{4+} , m , and Fe^{3+} , n , in the samples can be given as $m=p-r$ and $n=q+2r-2p$, since Fe^{4+} and Fe^{2+} react to form Fe^{3+} ($Fe^{4+} + Fe^{2+} \rightarrow 2Fe^{3+}$) in the solution.

2.4. Measurement of Electrical Properties

The d.c. electrical resistivity of the samples was measured at temperatures from 100 to 300 K by the three probe method [10]. The electrodes were formed by evaporating Au onto the surface of the pellets and connected to the leads with silver paste. The Seebeck coefficient of the $La_{1-x}Sr_{1+x}FeO_4$ samples was determined by measuring the electrical voltage produced between both ends of the pellet sample when one end of the sample was heated.

3. RESULTS

3.1. X-Ray Diffraction Analysis

The XRD patterns of the heat-treated samples of $La_{1-x}Sr_{1+x}FeO_4$ ($0 \leq x \leq 0.20$) are shown in Fig. 3. In the range $0 \leq x \leq 0.10$, the patterns show a single phase of K_2NiF_4 structure with the tetragonal $I4/mmm$ space group symmetry. On the other hand, the samples of $x \geq 0.15$ contain $Sr_2FeO_{4.8}$ as a second phase, which did not disappear even when heat-treatment at $1400^\circ C$ was prolonged up to 30 h. The color of the samples changed from dark brown for $x=0$ to black for

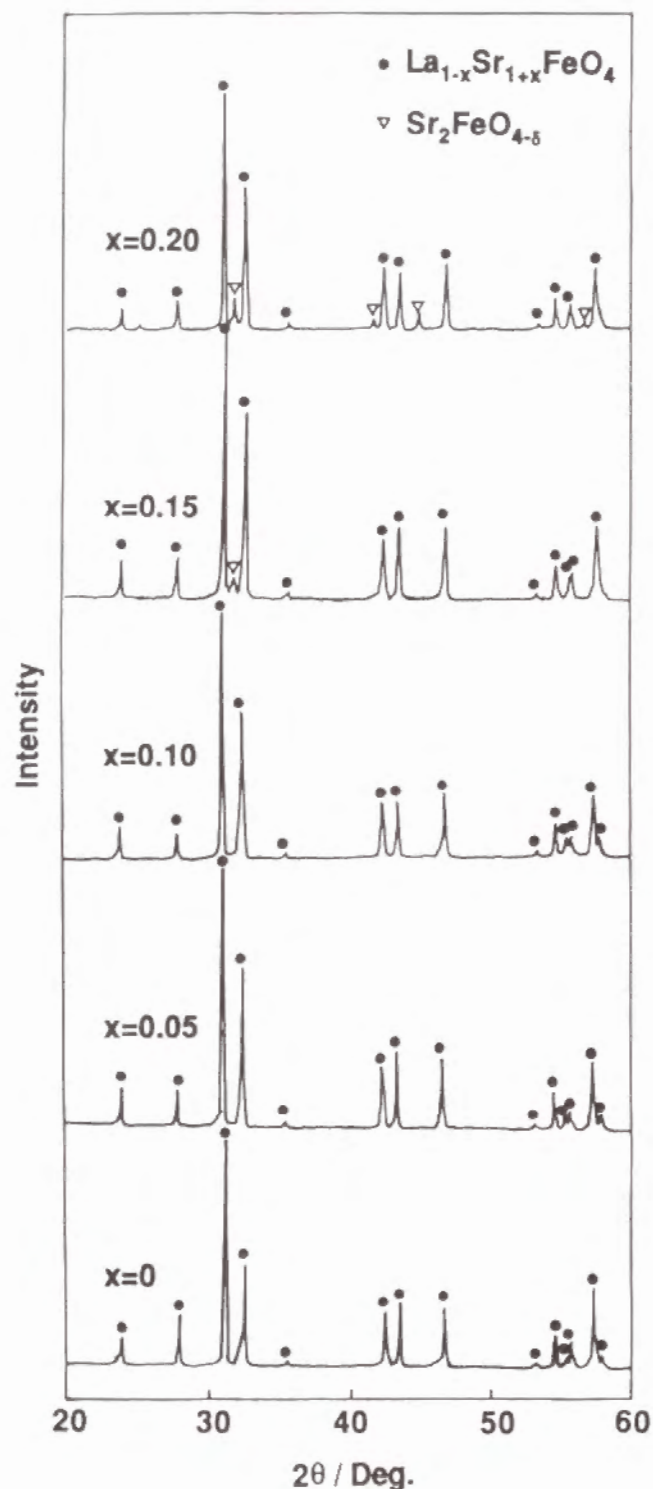


Fig. 3. The x-ray diffraction patterns of $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ in the range $0 \leq x \leq 0.20$ after heating at 1400°C for 20 h in air.

$x=0.05$ and 0.10 .

The XRD patterns of the heat-treated samples of $\text{La}_{1-x}\text{Ca}_x\text{SrFeO}_4$ and $\text{La}_{1-x}\text{Ba}_x\text{SrFeO}_4$ ($x=0.10, 0.15$) are shown in Fig. 4. The patterns of both the Ca and Ba substituted samples of $x=0.10$ show a single phase of the tetragonal $I4/mmm$ K_2NiF_4 structure. The samples of $x=0.15$ with Ca and Ba substitution contain $\text{Sr}_2\text{FeO}_{4-\delta}$ as a second phase, as in the case of the $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ samples.

The XRD patterns of the heat-treated samples of $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ in the range $0.10 \leq y \leq 0.30$ are shown in Fig. 5. The patterns of the samples of $y=0.10$ and 0.20 show a single phase of tetragonal $I4/mmm$ K_2NiF_4 structure, whereas the sample of $x=0.30$ contains a trace of Y_2O_3 as an impurity phase.

3.2. $\text{Fe}^{3+}/\text{Fe}^{4+}$ Ratio and Oxygen Content

The relative abundance (%) of Fe^{3+} and Fe^{4+} of the single-phase $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($x=0, 0.05, 0.10$ for $\text{A}=\text{Sr}$ and $x=0.10$ for $\text{A}=\text{Ca}, \text{Ba}$) samples are summarized in Table I, and the Fe^{4+} abundance is plotted against the calculated values in Fig. 6. The abundance of Fe^{4+} increases from 0.9 to 4.7 to 10.2 % with increasing x from 0 to 0.05 to 0.10 in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$. The abundances of Fe^{4+} of the Ca and Ba substituted samples with $x=0.10$ are 8.7 % and 9.6 %, respectively. The measured abundance of Fe^{4+} in $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ is in excellent agreement with the calculated one indicating that all the added divalent alkaline earth ions are substituted for trivalent La.

The oxygen content was calculated from the measured Fe^{3+} and Fe^{4+} abundances and the nominal composition, assuming that La, alkaline earths and O have the formal valence of +3, +2 and -2, respectively. The oxygen contents of all the single-phase $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ samples are calculated to be 4.00 and those of $\text{La}_{0.9}\text{Ca}_{0.1}\text{SrFeO}_4$ and $\text{La}_{0.9}\text{Ba}_{0.1}\text{SrFeO}_4$ to be 3.99 and 4.00,

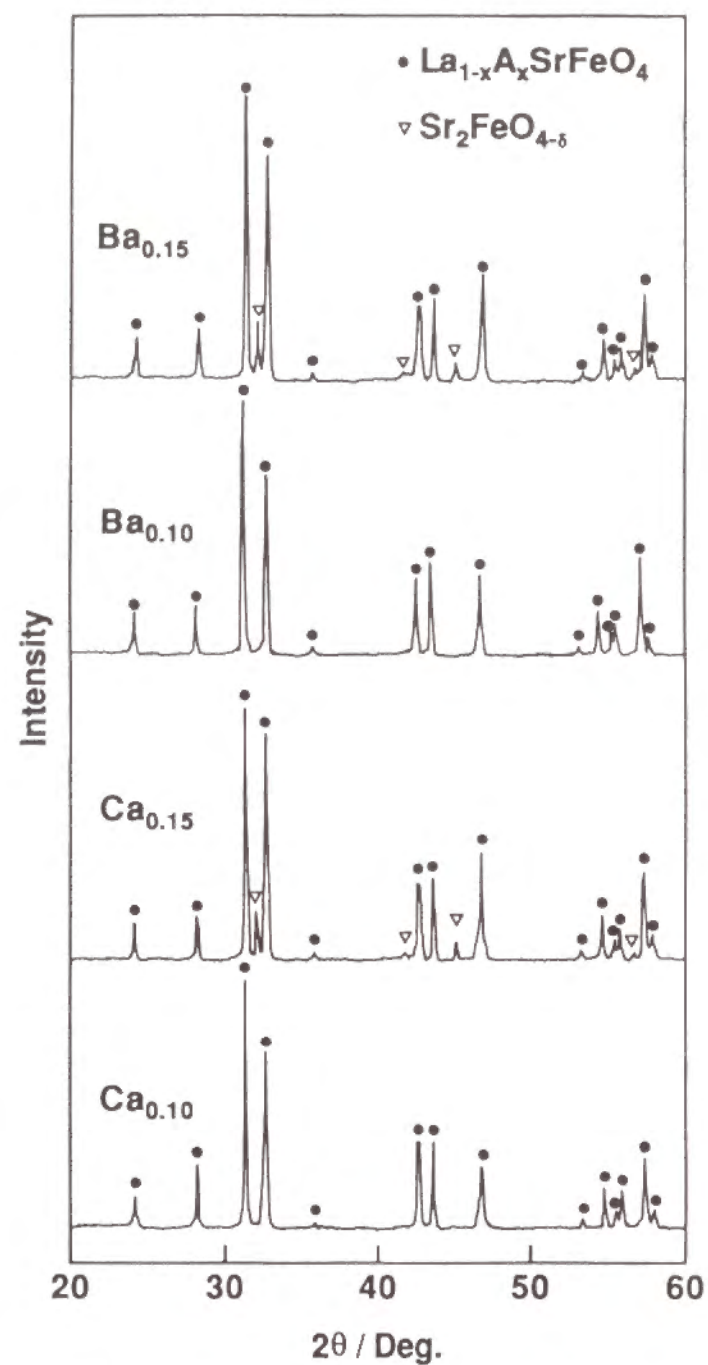


Fig. 4. The x-ray diffraction patterns of $\text{La}_{1-x}\text{Ca}_x\text{SrFeO}_4$ and $\text{La}_{1-x}\text{Ba}_x\text{SrFeO}_4$ at $x=0.10$ and 0.15 after heating at 1400°C for 20 h in air.

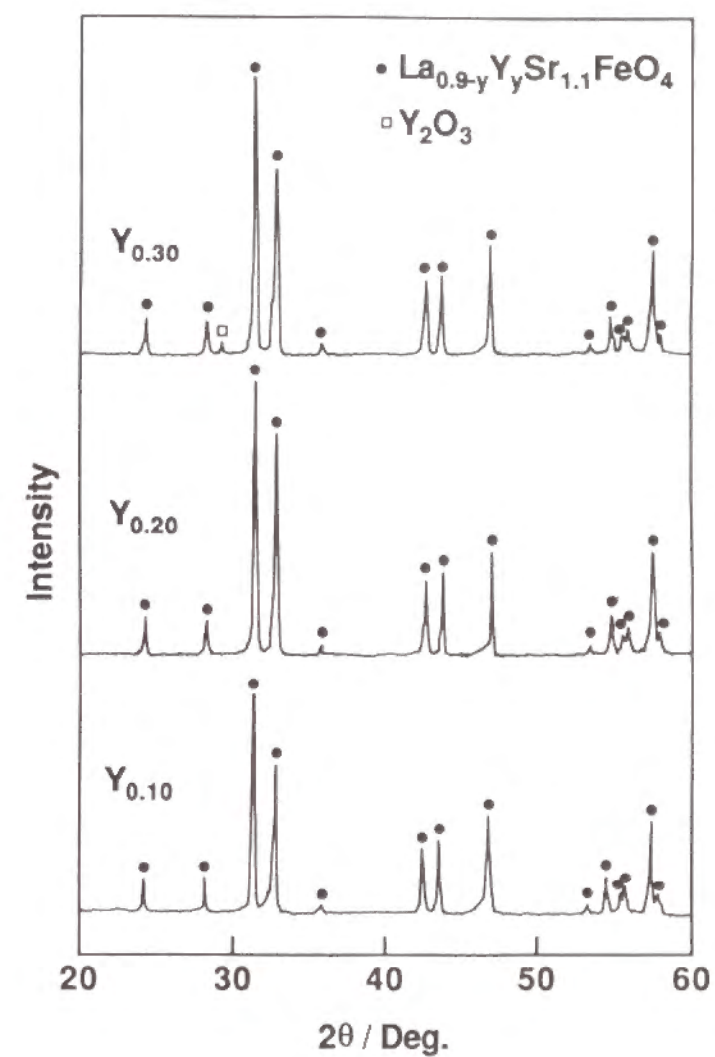


Fig. 5. The x-ray diffraction patterns of $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ in the range $0.10 \leq y \leq 0.30$ after heating at 1400°C for 20 h in air.

Table I The abundance of Fe³⁺ and Fe⁴⁺, oxygen content and lattice constants of the parent LaSrFeO₄ and the substituted La_{1-x}A_xSrFeO₄ (A=Sr, Ca and Ba) and La_{0.9-y}Y_ySr_{1.1}FeO₄ samples.

Sample (A _x , Y _y)	Abundance(%)		Oxygen Content	Lattice Constants / nm	
	Fe ³⁺	Fe ⁴⁺		<i>a</i>	<i>c</i>
LaSrFeO ₄	99.1	0.9	4.00	0.3876	1.2713
Sr _{0.05}	95.3	4.7	4.00	0.3873	1.2720
Sr _{0.10}	89.8	10.2	4.00	0.3868	1.2737
Sr _{0.15} ^a	-	-	-	0.3866	1.2745
Sr _{0.20} ^a	-	-	-	0.3865	1.2743
Ca _{0.10}	91.3	8.7	3.99	0.3868	1.2690
Ca _{0.15} ^a	-	-	-	0.3867	1.2684
Ba _{0.10}	90.4	9.6	4.00	0.3875	1.2750
Ba _{0.15} ^a	-	-	-	0.3876	1.2761
Y _{0.10}	-	-	-	0.3864	1.2704
Y _{0.20}	-	-	-	0.3861	1.2673

^a Not a single phase with K₂NiF₄ structure

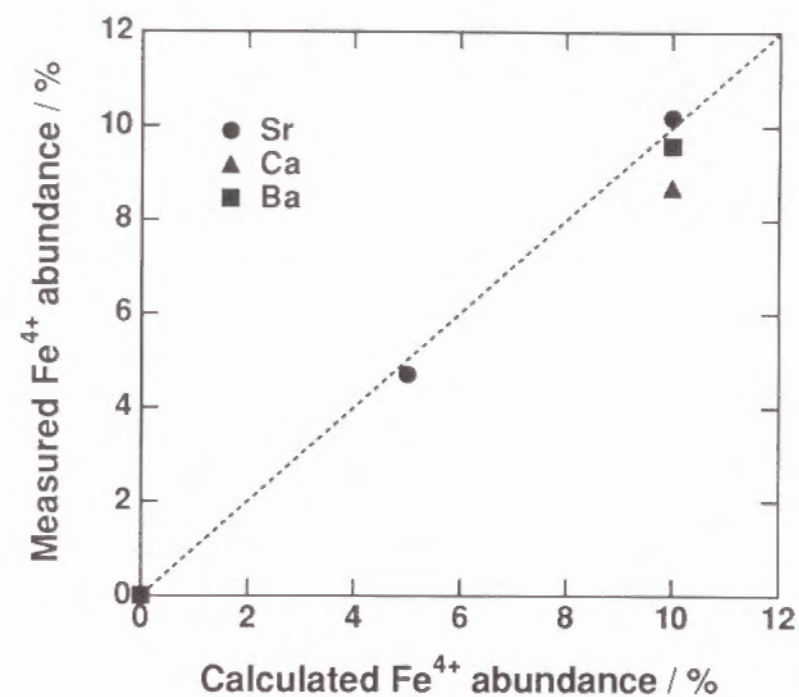


Fig. 6. The calculated and measured abundance of Fe⁴⁺ in La_{1-x}A_xSrFeO₄ (A=Ca, Sr, Ba).

respectively. These results indicate that the present ionic substitution does not cause the formation of oxygen vacancies.

3.3. Lattice Constants

The lattice constants a and c of the $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ samples are plotted against x in Fig. 7 and summarized in Table I. The experimental error of these values is within 0.05 %. The lattice constants of the parent LaSrFeO_4 obtained in the present work, $a=0.3876$ nm and $c=1.2713$ nm, agree well with those reported by Shimada and Koizumi [11]. As seen in Fig. 7, the lattice constant a decreases while c increases monotonically with increasing x in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$. The rate of their change with x from 0 to 0.10 is 0.21 % for a and 0.19 % for c . In the range $x>0.10$, where the samples contain impurity phases, the change in the lattice constants becomes smaller, which is partially because of the imperfect solubility of Sr in the compound for $x>0.10$.

Both of the lattice constants a and c decrease monotonically with increasing x in $\text{La}_{1-x}\text{Ca}_x\text{SrFeO}_4$. In contrast, the lattice constant a is nearly constant and c increases with increasing x in $\text{La}_{1-x}\text{Ba}_x\text{SrFeO}_4$. The rate of decrease in the lattice constant a for the Ca-substituted sample is 0.21 % in the range $0\leq x\leq 0.10$. The rate of change in the lattice constant c is 0.18 % (decrease) for the Ca and 0.29 % (increase) for the Ba substituted sample in the range $0\leq x\leq 0.10$.

The lattice constants a and c of the $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ samples are summarized in Table I. Figure 8 shows the change in the lattice constants of $\text{La}_{1-(x+y)}\text{Y}_y\text{Sr}_{1+x}\text{FeO}_4$ with x and y in the range $0\leq x\leq 0.10$ at $y=0$ and $0.10\leq y\leq 0.20$ at $x=0.10$. It is seen that the lattice constant a , which decreases with increasing x in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ from 0 to 0.10, continues to decrease with increasing y in $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ from 0 to 0.20. On the contrary, the lattice constant c , which

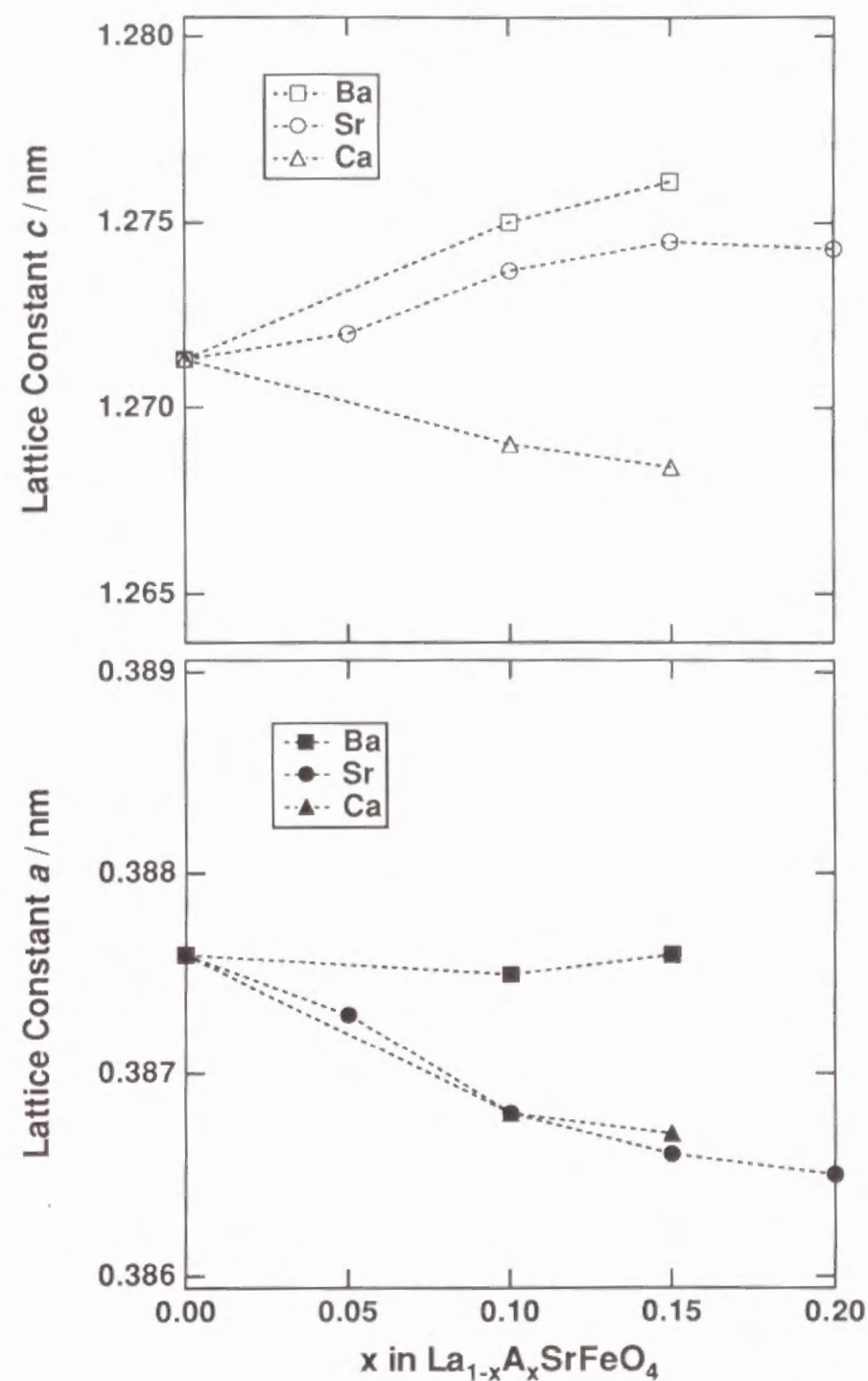


Fig. 7. Variation of the lattice constants a and c as a function of x in a series of $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$.

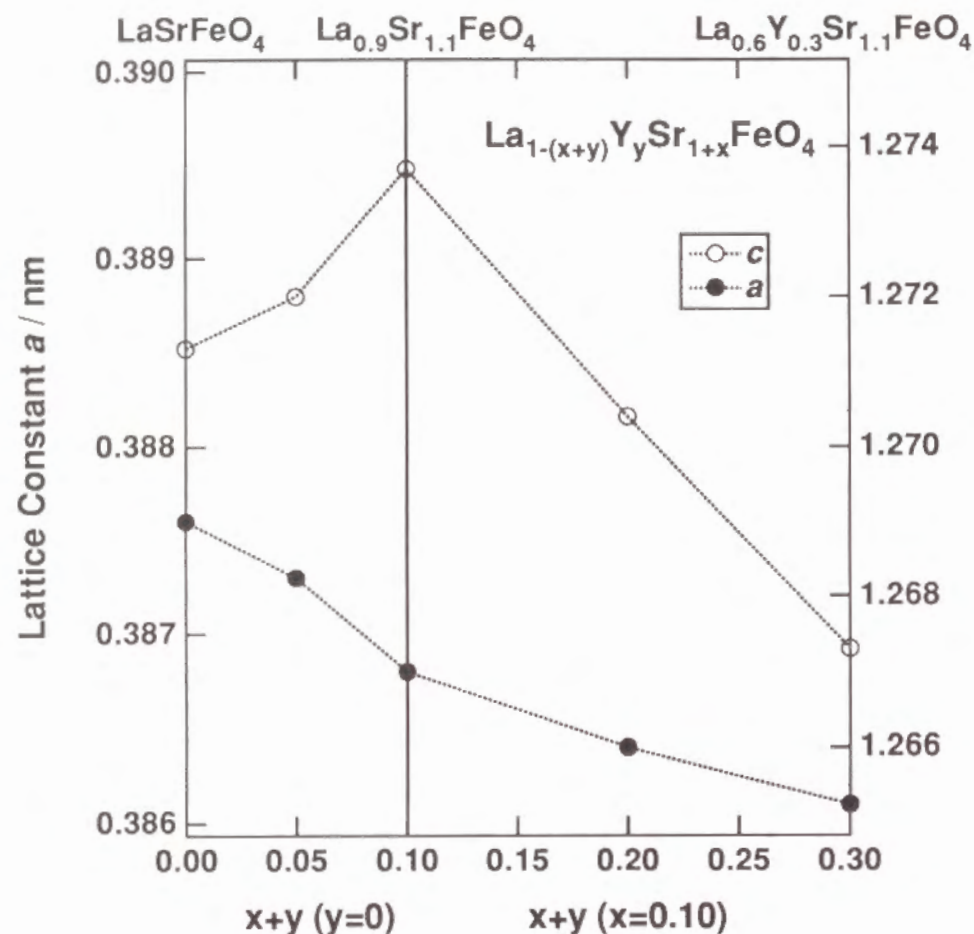


Fig. 8. Variation of the lattice constants a and c as a function of x and y in a series of $\text{La}_{1-(x+y)}\text{Y}_y\text{Sr}_{1+x}\text{FeO}_4$.

increases with x , turns to decrease with increasing y in the range $0 \leq y \leq 0.20$. The rate of decrease in the lattice constants is 0.18 % for a and 0.50 % for c with increasing y from 0 to 0.20.

3.4. Electrical Properties

As summarized in Table II, the resistivity of $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ at 300 K is $1.15 \times 10^5 \Omega\text{-cm}$ for $x=0$, $2.21 \times 10^3 \Omega\text{-cm}$ for $x=0.05$ and $6.81 \times 10^2 \Omega\text{-cm}$ for $x=0.10$, which shows a monotonical decrease with increasing x . The resistivity of $\text{La}_{0.9}\text{Ca}_{0.1}\text{SrFeO}_4$ and $\text{La}_{0.9}\text{Ba}_{0.1}\text{SrFeO}_4$ at 300 K is $6.72 \times 10^2 \Omega\text{-cm}$ and $8.99 \times 10^1 \Omega\text{-cm}$, respectively. Figure 9, 10 and 11 show Arrhenius plots of $\log \rho$ vs. $1/T$, where ρ is the resistivity and T is the absolute temperature, for a series of $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$, $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ ($A=\text{Ca}, \text{Sr}, \text{Ba}$) and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$, respectively. Temperature dependences of the resistivity for all the samples indicate semiconducting behavior with $d\rho/dT < 0$.

Since straight lines have been given by an Arrhenius plot in the temperature range employed in the present measurements as seen in Fig. 9, 10 and 11, the apparent activation energy for conduction, E_a , can be calculated from the plots using the following Eq. (1),

$$\ln \rho = E_a / 2k_B T + C \quad \dots (1)$$

where k_B is a Boltzmann constant and C is a constant. The E_a values are summarized in Table II and those of the $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ and $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ samples are plotted against x and the kinds of A, respectively, in Fig. 12 (a) and (b). It is seen that E_a decreases monotonically with increasing x in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$. On the other hand, the value of E_a hardly depends on the kinds of

Table II Electrical properties of $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ (A=Sr, Ca and Ba) and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$; ρ : resistivity, E_a : activation energy for conduction, Q : Seebeck coefficient.

Sample (A_x, Y_y)	$\rho / \Omega\text{-cm}$	E_a / eV	Q / mVK^{-1}
LaSrFeO_4	1.15×10^5	0.338	0.175
$\text{Sr}_{0.05}$	2.21×10^3	0.306	0.152
$\text{Sr}_{0.10}$	6.81×10^2	0.281	0.141
$\text{Ca}_{0.10}$	6.72×10^2	0.276	0.147
$\text{Ba}_{0.10}$	8.99×10^1	0.276	0.140
$\text{Y}_{0.10}$	-	0.289	-
$\text{Y}_{0.20}$	-	-	0.155

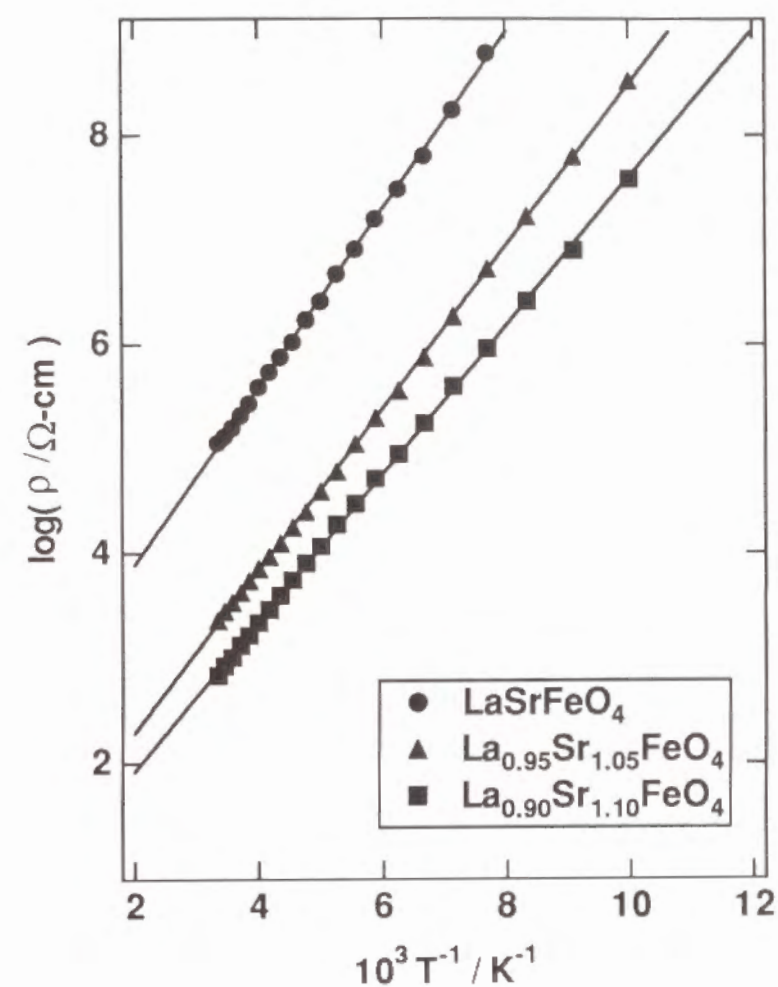


Fig. 9. Log ρ vs. $1/T$ plot in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$ with $x=0, 0.05$ and 0.10 .

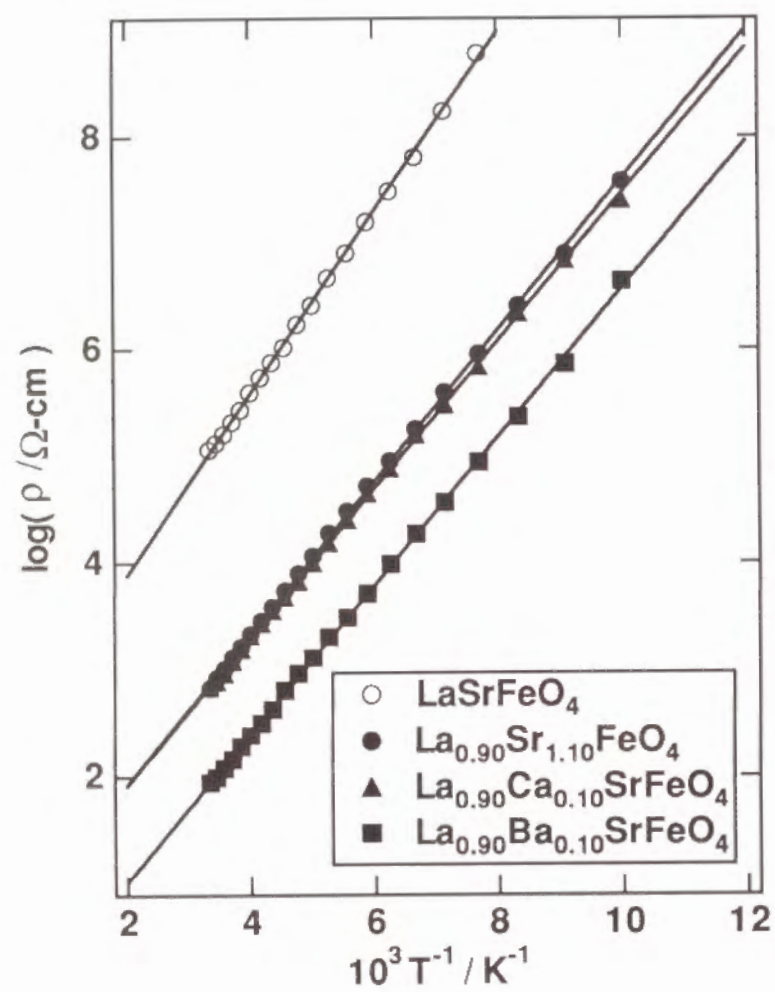


Fig. 10. Log ρ vs. $1/T$ plot in $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ with $\text{A}=\text{Ca}$, Sr and Ba .

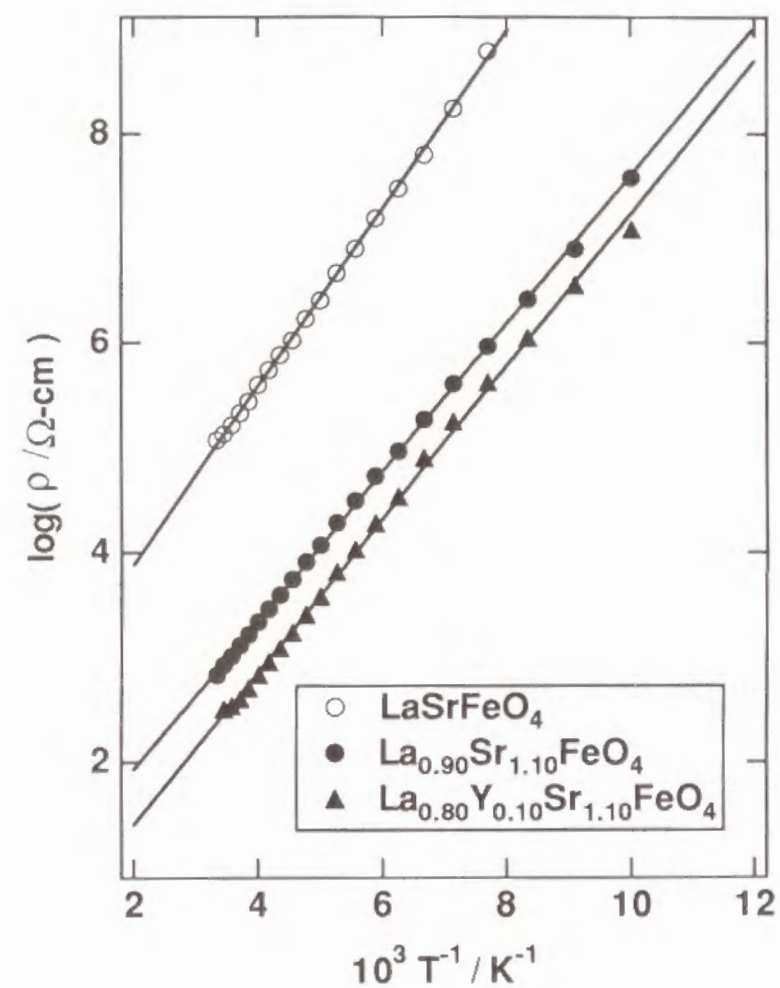


Fig. 11. Log ρ vs. $1/T$ plot in $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ with $y=0$ and 0.10 .

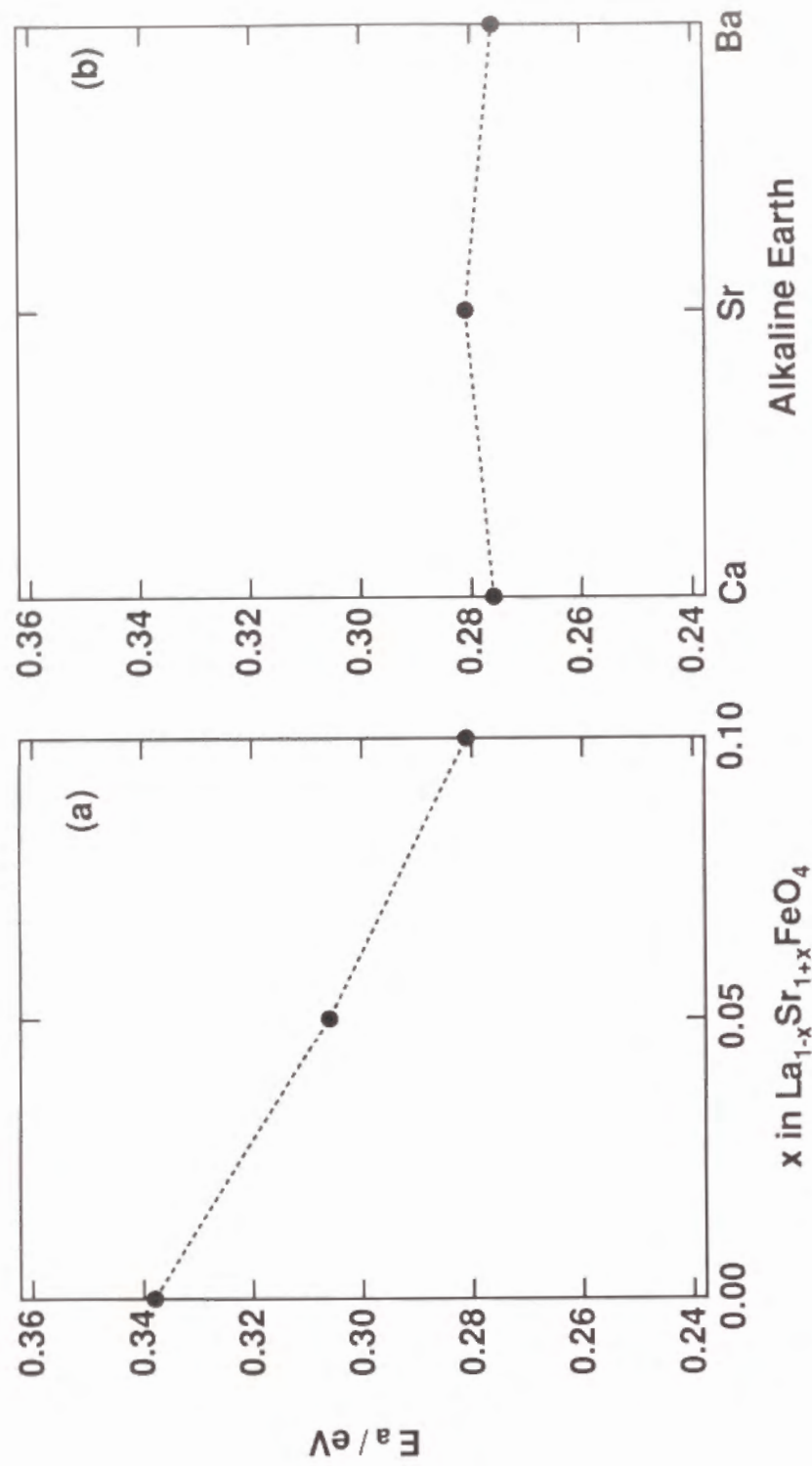


Fig. 12. Dependences of the activation energy for conduction on x in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$ (a), and on the type of the alkaline earth metals in $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ (b).

alkaline earths in $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$.

The Seebeck coefficient Q was determined from the following Eq. (2) [12],

$$Q = \frac{dV}{dT} = -\frac{V_h - V_c}{T_h - T_c} \quad \dots (2)$$

where $V_h - V_c$ and $T_h - T_c$ are the electromotive force and temperature difference between the hot and cold ends of the sample, respectively. Figure 13 shows Seebeck coefficient Q of the samples $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$ as a function of x , and the values of Seebeck coefficient Q of the samples are summarized in Table II. All the Q values are positive. In $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$, Q decreases monotonically with increasing x .

4. DISCUSSION

4.1. Changes in the Lattice Constants by Ionic Substitution

The decrease in the lattice constant a with increasing x as observed in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$ cannot be explained by the difference in ionic radius between La^{3+} and Sr^{2+} since Sr^{2+} has a larger ionic radius (0.131 nm) than La^{3+} (0.1216 nm) [13]. A tentative interpretation can be made on the basis of the electronic state of the Fe ions and the crystal structure featured by two-dimensionally linked FeO_6 octahedra. The models of the FeO_6 octahedra with Fe^{3+} or Fe^{4+} are shown in Fig. 14. The FeO_6 octahedra containing Fe^{3+} ions in the parent LaSrFeO_4 do not undergo Jahn-Teller distortion because they have five 3d electrons in a high-spin state [14], three of which lie in lower t_{2g} orbitals and two of which in higher e_g orbitals. However, when one electron is removed

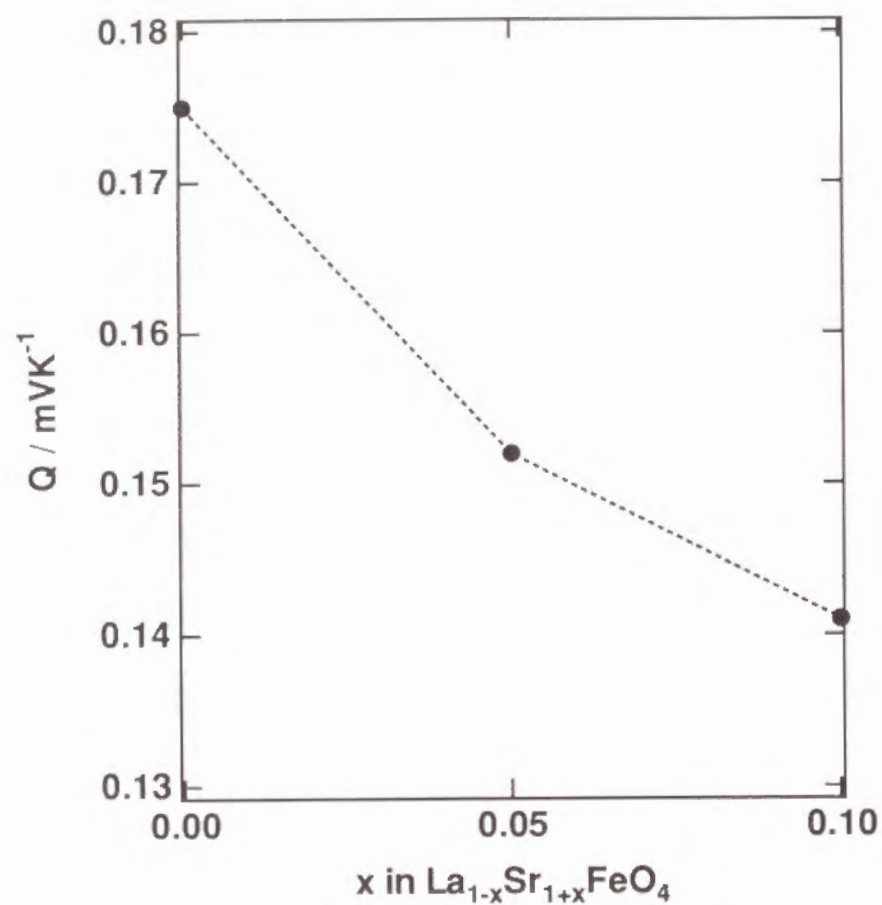


Fig. 13. Dependence of Seebeck coefficient on x in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$.

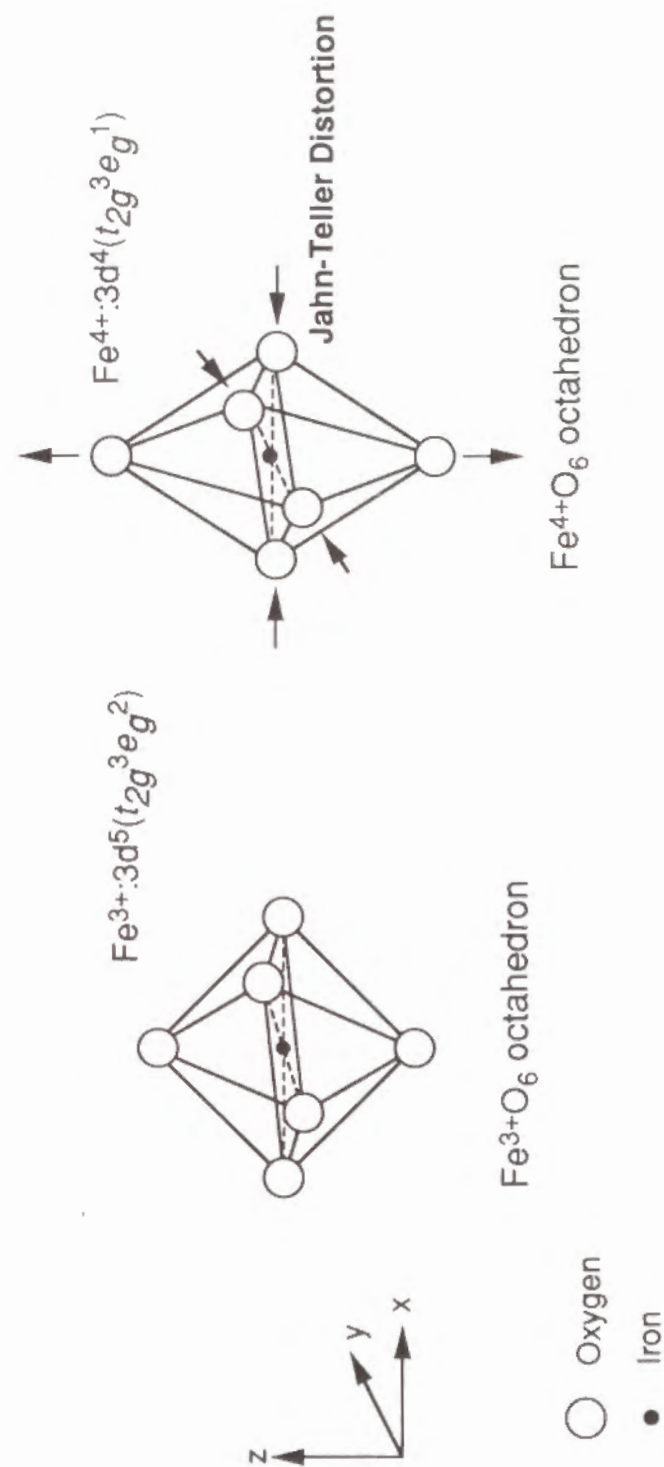


Fig. 14. The model for the FeO_6 octahedron with Fe^{3+} or Fe^{4+} ion.

from the e_g orbital of Fe^{3+} ion to form Fe^{4+} ion, and the introduced hole and the other retained e_g electron are localized at the Fe^{4+} ion, the Fe(IV)O_6 octahedron should undergo Jahn-Teller distortion with contraction in x-y plane and expansion in z direction. The decrease in the lattice constant a and the increase in c observed in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ with increasing x are therefore considered to be caused by the Jahn-Teller distortion of the FeO_6 octahedra. The localization of holes on the Fe ions is likely to occur in the K_2NiF_4 structure featured by the strong two-dimensionality, in contrast to the three dimensional perovskite SrFeO_3 , which does not exhibit Jahn-Teller distortion because of the itinerant nature of e_g electrons [15].

The rate of decrease in the lattice constant a as observed in $\text{La}_{1-x}\text{Ca}_x\text{SrFeO}_4$ is much larger than expected from the slightly smaller ionic radius of Ca^{2+} (0.118 nm) than La^{3+} (0.1216 nm). This is also thought to result from the distorted FeO_6 octahedra by Jahn-Teller effect. Little change in the lattice constant a in $\text{La}_{1-x}\text{Ba}_x\text{SrFeO}_4$ may be attributed to the compensating effects of the larger ionic radius of Ba^{2+} (0.147 nm) and Jahn-Teller distortion, which would expand and contract the a -axis, respectively.

Differing from the case for the lattice constant a , the decrease in the lattice constant c with increasing x in $\text{La}_{1-x}\text{Ca}_x\text{SrFeO}_4$ and the increase in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ and $\text{La}_{1-x}\text{Ba}_x\text{SrFeO}_4$ can be appropriately explained by the differences in the ionic radius of the alkaline earth ions. Because LaSrFeO_4 is composed of two (La, Sr)O and one FeO_2 layers stacked alternatively along the c -axis as shown in Fig. 1, the size of the cations in the (La, Sr)O layers is expected to affect more significantly the lattice constant c than the lattice constant a . That is, larger ions such as Sr^{2+} and Ba^{2+} that are substituted for La^{3+} elongate the interlayer distance while smaller ions such as Ca^{2+} shorten it, which results in

the observed change in the lattice constant c .

A comparison of the three samples of $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$), which differ only in the kind of alkaline earth, exhibits clearly the effect of the ionic radius on the structure. The lattice constants a and c show a 0.18 and 0.47 % increase, respectively, with increasing ionic radius from 0.118 (Ca^{2+}) to 0.147 nm (Ba^{2+}). The smaller increasing rate of a is possibly due to the stiff Fe-O bond in the two-dimensional FeO_2 planes, which makes the lattice constant a difficult to change. In contrast, the larger increasing rate of c reflects that the lattice constant c easily changes by the substitution of ions with different ionic radii.

As shown in Fig. 8, the decrease in the lattice constants a and c in $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ on changing y from 0 to 0.20 is thought to result principally from the smaller ionic radius of Y^{3+} (0.1075 nm) than that of La^{3+} (0.1216 nm) because the substitution of Y^{3+} for La^{3+} does not cause the valence change of Fe which affects the electronic structure. The rate of decrease in the lattice constants is 0.18 % for a and 0.50 % for c with increasing y from 0 to 0.20. Such a difference can be also interpreted by the same reason as mentioned above.

4.2. Changes in the Electrical Properties by Ionic Substitution

The $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ samples were found to exhibit semiconducting behavior and their resistivity decreased with increasing x . The activation energy for conduction E_a showed a monotonical decrease with increasing x . The sign of the charge carrier and the change in the carrier concentration can be known from the Seebeck coefficient [12]. The Seebeck coefficient Q is expressed by the following Eq. (3) when the electrical conductivity is ascribed to a single kind of carrier [12],

$$Q = \pm \frac{k_B}{e} \left(\frac{E_F}{k_B T} + A \right) = \pm \frac{k_B}{e} \left(\ln \frac{N}{c} + A \right) \dots (3)$$

where E_F is the energy gap between the Fermi level and the transport level, bottom of the conduction band (n-type) or top of the valence band (p-type), A is the energy transport term, N is the effective density of states at the transport level, and c is the carrier concentration. The observed positive Q values indicate that the conduction carriers in the present $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ samples are holes. The observation that Q decreases with x suggests that the number of carriers increases with increasing x . In other words, the number of holes increases with increasing Fe^{4+} formed by charge compensation in substituting Sr^{2+} for La^{3+} . It can be concluded, therefore, that the decrease in the resistivity of $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ with increasing x results from the increase in the carrier concentration and the decrease in the activation energy for conduction. Adler [16] has studied quite recently on the properties of the K_2NiF_4 -type $\text{Sr}_2\text{FeO}_{4.8}$, which corresponds to the composition of $x=1$ in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$, with 88 % of Fe^{4+} in abundance. According to his report, $\text{Sr}_2\text{FeO}_{4.8}$ exhibits semiconducting behavior and has the activation energy E_a of 0.18 eV, which is smaller than those of the present $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ samples (0.338 eV for $x=0$ and 0.281 eV for $x=0.10$). It can be expected, therefore, that $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ will exhibit semiconducting behavior and E_a will continue to decrease with increasing Fe^{4+} content in the whole range of x .

The change in the activation energy for conduction E_a of LaSrFeO_4 by the substitution is considered to result from the change in the electronic structure around the Fermi level, which is composed of the $\text{Fe-}3d_{x^2-y^2}$ and $\text{O-}2p_\sigma$ bands. Since the $\text{Fe-}3d_{x^2-y^2}$ and $\text{O-}2p_\sigma$ are the x-y components of the bands, the Fe-O

distance and angle in the FeO_2 planes, which determine the lattice constant a , are thought to affect the band structure. The decrease in E_a with increasing x observed in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$, therefore, is expected to result from the change in electronic structure due to the decrease in the lattice constant a as well as the increase in the number of holes in the $\text{Fe-}3d_{x^2-y^2}$ or $\text{O-}2p_\sigma$ bands. E_a values of the three $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$) samples, however, were hardly dependent on the kind of alkaline earths, although the lattice constant a of $\text{La}_{0.9}\text{Ba}_{0.1}\text{SrFeO}_4$ (0.3875 nm) is larger than that of $\text{La}_{0.9}\text{Ca}_{0.1}\text{SrFeO}_4$ (0.3868 nm) and $\text{La}_{0.9}\text{Sr}_{1.1}\text{FeO}_4$ (0.3868 nm). In addition, E_a values of the $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ samples are also almost unchanged with increasing y , as shown in Table II, although the lattice constant a decreases monotonically with increasing y . It is thought, in consequence, that the change in the lattice constant a (0.18%) attained in the present $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$ is too small to change the electronic structure and accordingly the activation energy for conduction. Thus the decrease in E_a with increasing x in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$ is ascribed to the change in the electronic structure mainly due to the increase in the hole concentration. In case of the lattice constant c , because of the two-dimensional feature of the electronic structure around Fermi level in the x-y plane as mentioned above, even the relatively large increase (0.47 % for $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ and 0.50 % for $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$) does not affect the activation energy.

The resistivities of the three $\text{La}_{0.9}\text{A}_{0.1}\text{SrFeO}_4$ samples, 6.72×10^2 , 6.81×10^2 and $8.99 \times 10^1 \Omega\text{-cm}$ for $\text{La}_{0.9}\text{Ca}_{0.1}\text{SrFeO}_4$, $\text{La}_{0.9}\text{Sr}_{1.1}\text{FeO}_4$ and $\text{La}_{0.9}\text{Ba}_{0.1}\text{SrFeO}_4$, respectively, corresponded neither to the change in the activation energy for conduction, which is independent of the kind of alkaline earths as shown in Fig. 12 (b), nor to that in the Seebeck coefficient, which is almost constant as

shown in Table II.

5. CONCLUSION

The formation, lattice constants and electrical properties of the LaSrFeO_4 system with substitution of alkaline earths or Y for La were studied, and the following results were obtained.

Single-phase compounds with the K_2NiF_4 structure were obtained in the range $0 \leq x \leq 0.10$ and $0 \leq y \leq 0.20$ for $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$) and $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$, respectively. From the EDTA titration, it was shown that Fe^{3+} was oxidized to Fe^{4+} in an amount corresponding to the substituted alkaline earth ion, resulting in a $\text{Fe}^{3+}/\text{Fe}^{4+}$ mixed valence state. The lattice constant a decreased monotonically with increasing x for $\text{A}=\text{Ca}$ and Sr and was almost unchanged for $\text{A}=\text{Ba}$, whereas c decreased with increasing x for $\text{A}=\text{Ca}$ and increased for $\text{A}=\text{Sr}$ and Ba . In $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$, both the lattice constants a and c decreased with increasing y .

The electrical conductivity of all the substituted LaSrFeO_4 samples was semiconducting in the temperature range of 100 - 300 K, and the resistivity decreased with increasing Fe^{4+} , which was considered to result from the increase in the carrier (hole) concentration, as evidenced by the Seebeck coefficient measurement and the decrease in the activation energy. The activation energy for conduction decreased with increasing x or with increasing Fe^{4+} in $\text{La}_{1-x}\text{Sr}_x\text{FeO}_4$. The change in the lattice constant a without changing the Fe^{4+} content, however, did not cause the change in the activation energy in the present samples.

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SUMMARY

The synthesis, properties and chemical modification of superconducting oxides have been studied with a view to developing a new process of preparation, elucidating the mechanism of high temperature superconductivity, modifying the crystal and electronic structure of superconductors and designing chemically new superconducting materials. The copper oxide-based superconductors, $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, have been investigated in the context of prior work on the synthesis and structure. The 3d transition metal oxides, NdNiO_{3-y} and LaSrFeO_4 , have been investigated in search for new superconducting materials. The application of the sol-gel method to the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ and NdNiO_{3-y} has opened up a new process for the preparation of superconducting oxides. Chemical designing of superconducting materials has been carried out by means of chemical modification of $\text{YBa}_2\text{Cu}_4\text{O}_8$, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, NdNiO_{3-y} and LaSrFeO_4 , on the basis of the crystal structure and electronic structure of many metal oxides.

In Chapter 1, the results of the application of the sol-gel technique to the preparation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ superconductor have been presented. In Section 1, it has been found that a pure single phase of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y-124) is successfully obtained by heating a gel powder, which is made from an aqueous solution of metal acetates and tartaric acid, in flowing oxygen. The optimum temperature

of the heat-treatment to produce the Y-124 phase is 780 °C. Heating the gel powder at 780 °C for 30 h results in formation of a single phase of the Y-124 with no impurity peaks observed in the XRD pattern, showing T_c of 80 K in the susceptibility measurements. The pellet made of this powder sample shows T_c (onset) at 87 K and T_c (end) at 78 K in the resistance measurements. The pellet, which is made from the gel powder heated at 780 °C for 10 h, is a pure single phase of the Y-124 showing T_c (onset) of 85 K and T_c (end) of 75 K, when it is sintered at 780 °C for 30 h. In Section 2, the mechanism of the formation of $\text{YBa}_2\text{Cu}_4\text{O}_8$ from the acetate-derived gel has been investigated. It has been shown that there are two key routes for the formation of the Y-124 phase; one is the reaction between the tetra-I Y-123 phase and CuO, and the other the reaction between $\text{Y}_2\text{Cu}_2\text{O}_5$ and $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$. The formation of the tetra-I phase Y-123, which cannot be prepared by the conventional solid-state reaction under ambient pressure, and the rapid formation of highly oxidized $\text{Ba}_2\text{Cu}_3\text{O}_{5.9}$ result in the formation of the Y-124 phase in a relatively low O_2 pressure of 1 atm.

Chapter 2 describes the effects of the chemical substitution to $\text{YBa}_2\text{Cu}_4\text{O}_8$ in terms of the changes in structure and properties. In Section 1, single-phase $\text{YBa}_{2-x}\text{R}_x\text{Cu}_4\text{O}_8$ (R=Sr, K, Na) superconductors have been successfully prepared by the sol-gel method and the effects of the partial substitution of Sr^{2+} , K^+ or Na^+ for Ba^{2+} on the structure and properties of $\text{YBa}_2\text{Cu}_4\text{O}_8$ have been discussed. The lattice constants a , b and c of the Sr-substituted Y-124 phase monotonically decrease with increasing Sr concentration. The slight increase in T_c (onset) and T_c (end) observed at $x=0.2$ is attributed to the lattice contraction in the CuO_2 plane. The lattice constant a of the K-substituted Y-124 phase slightly decreases while b and c do not change with increasing K concentration. The oxygen content decreases and T_c hardly changes with substitution of K. An expected

increase in T_c by hole doping cannot be achieved because of the formation of oxygen vacancies. The lattice constant a of the Na-substituted Y-124 phase decreases while b and c do not change with increasing Na concentration. The oxygen content decreases and T_c (onset) hardly changes with substitution of Na. T_c (end), however, rises by 4 K, probably due to the lattice contraction in the CuO_2 plane and/or the decrease in the weak link of grain boundaries. Grain growth and change in the shape of the grains from particulate to plate-like ones are observed in the K- and Na-substituted Y-124 samples. In Section 2, the effects of the Li substitution on the formation, structure and superconducting properties have been examined. A single phase of the Y-124 is obtained in the range $0 \leq x \leq 0.08$ in $\text{YBa}_2\text{Cu}_{4-x}\text{Li}_x\text{O}_8$, while impurity phases appear when x exceeds 0.08. The lattice constants are almost invariant with increasing x , probably due to the similar ionic radius between Cu^{2+} and Li^+ . The superconducting transition temperature decreases monotonically with increasing Li content. The deterioration of superconductivity by the replacement of Cu with Li is attributed to the impurity effect in the CuO_2 planes, which gives rise to the magnetic moment.

In chapter 3, the synthesis and properties of one of the rare earth nickel oxides, NdNiO_{3-y} , have been presented. It has been shown that the oxygen-deficient NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$ with a perovskite structure are successfully prepared under ambient pressure by the sol-gel method starting with metal acetates, EDTA and water. Single-phase materials are obtained in relatively short time of 20 h by heating at 700 °C in flowing oxygen. The amount of oxygen defects, y , is 0.24 for NdNiO_{3-y} and 0.23 for $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$, which results in the mixed valence state of $\text{Ni}^{2+}/\text{Ni}^{3+}$ in the sample as evidenced by the XPS measurement on Ni. The temperature dependent metal-semiconductor

transition is observed at 130 and 240 K for NdNiO_{3-y} and $\text{Nd}_{0.9}\text{Y}_{0.1}\text{NiO}_{3-y}$, respectively. The increase in the metal-semiconductor transition temperature by the substitution of Y for Nd is attributed to the decrease in the lattice constants, which results in the more bent Ni-O-Ni bond and hence the narrower bandwidth of Ni-3d and O-2p bands.

In Chapter 4, the replacement of oxygen by sulfur has been attempted in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system, and the changes in the crystal structure and electrical properties have been discussed. In Section 1, the results of the sulfur-substitution of the $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_4$ superconductor have been shown. It has been found that superconductivity is degraded as the sulfur concentration increases in $\text{La}_{1.84}\text{Sr}_{0.16}\text{CuO}_{4-y}\text{S}_y$, that is, superconducting transition temperature T_c decreases, semiconducting behavior appears at low temperatures and the electrical resistance increases with increasing sulfur concentration. The crystal structure at room temperature changes from tetragonal to orthorhombic, and the in-plane lattice constants increase and the c -axis shrinks with increasing sulfur content. These features of changes in the crystal structure and electrical properties are quite similar to those observed in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ system with strontium content decreasing from $x=0.16$ to zero. In Section 2, the effects of sulfur-substitution on the structure and properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ ($x=0.26, 0.30$) have been studied. The lattice constants of $\text{La}_{1.74}\text{Sr}_{0.26}\text{CuO}_{4-y}\text{S}_y$ are almost unchanged in the range from $y=0$ to $y=0.16$, which indicates that sulfur substitution causes the change in electronic state rather than in structure. The sulfur-substituted materials exhibit superconducting transition at 37-39 K and the larger Meissner volume fraction than the materials with no sulfur addition. It is considered that the sulfur substitution reduce the excessive hole concentration of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ at higher Sr concentration, giving rise to the optimum hole concentration for the appearance

of superconductivity. Consequently, the region in which $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ shows superconductivity shifts to higher Sr concentrations with increasing sulfur content y .

Chapter 5 describes the formation, structure and electrical properties of the K_2NiF_4 -type LaSrFeO_4 system with substitution of alkaline earths or Y for La. Single-phase compounds with the K_2NiF_4 structure are obtained in the range of $0 \leq x \leq 0.10$ for $\text{La}_{1-x}\text{A}_x\text{SrFeO}_4$ ($\text{A}=\text{Ca}, \text{Sr}, \text{Ba}$) and $0 \leq y \leq 0.20$ for $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$. The Fe^{3+} ions are oxidized to Fe^{4+} in an equivalent amount of the substituted alkaline earth ion, resulting in a $\text{Fe}^{3+}/\text{Fe}^{4+}$ mixed valence state. The lattice constant a decreases monotonically with increasing x for $\text{A}=\text{Ca}$ and Sr and is almost unchanged for $\text{A}=\text{Ba}$, whereas c decreases with increasing x for $\text{A}=\text{Ca}$ and increases for $\text{A}=\text{Sr}$ and Ba . In $\text{La}_{0.9-y}\text{Y}_y\text{Sr}_{1.1}\text{FeO}_4$, both the lattice constants a and c decrease with increasing y . The electrical conductivity of all the substituted LaSrFeO_4 samples is semiconducting in the temperature range of 100 - 300 K, and the resistivity decreases with increasing Fe^{4+} , which is considered to result from the increase in the carrier (hole) concentration, as evidenced by the Seebeck coefficient measurement and the decrease in the activation energy. The activation energy for conduction decreases with increasing x or with increasing Fe^{4+} in $\text{La}_{1-x}\text{Sr}_{1+x}\text{FeO}_4$. The change in the lattice constant a without changing the Fe^{4+} content, however, does not cause the change in the activation energy in the present case.

LIST OF PUBLICATIONS

Chapter 1

S. Fujihara, H. R. Zhuang, T. Yoko, H. Kozuka, and S. Sakka, "Preparation of superconducting $\text{YBa}_2\text{Cu}_4\text{O}_8$ by the Sol-Gel Method", *Journal of Materials Research* **7** [9], 2355-2359 (1992).

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Chapter 2

S. Fujihara, T. Nakata, H. Kozuka, and S. Sakka, "Effects of Substitution of Sr, K or Na for Ba on the Structure and Properties of Gel-Derived $\text{YBa}_2\text{Cu}_4\text{O}_8$ Superconducting Oxide", *Bulletin of the Institute for Chemical Research, Kyoto University* **72** [2], 167-177 (1994).

S. Fujihara, H. Kozuka, and T. Yoko, "Superconducting Properties of the Li-Substituted $\text{YBa}_2\text{Cu}_4\text{O}_8$ Prepared by the Sol-Gel Method", to be submitted.

Chapter 3

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Chapter 4

H. Kozuka, S. Fujihara, T. Yoko, and S. Sakka, "Effect of Sulfur Doping on the Structure and Properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ Superconductor" *Japanese Journal of Applied Physics* **29** [9], L1608-L1611 (1990).

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Chapter 5

S. Fujihara, T. Nakata, H. Kozuka, and T. Yoko, "Effects of Substitution of Alkaline Earths or Y for La on Structure and Electrical Properties of LaSrFeO_4 ", *Journal of Solid State Chemistry*, in press.

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