

Mild synthesis of a $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor using a sol–gel method

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A $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor was obtained under atmospheric pressure using a sol–gel method. A material including this superconductive phase showed diamagnetic behaviour from 45 K and a drastic decrease of resistance from 51 K. It was found from X-ray diffraction and high-resolution transmission electron microscopy studies that the superconductive crystal has a tetragonal symmetry of $a = 0.382$ nm and $c = 1.129$ nm, and no superstructural ordering was found. However, we cannot completely rule out the possibility of carbon contamination on copper sites. It has been demonstrated that the sol–gel method is a promising route to synthesize high pressure phases of cuprate superconductors.

1. Introduction

The sol–gel method offers the possibility of introducing reactive precursors, the chemical structure of precursors (sols/gels) being designed for the final material. Therefore, we think that the sol–gel method is a promising route to synthesize the so-called high pressure phases of oxide superconductors under mild conditions such as atmospheric pressure. The high pressure phases are thought to be obtained without high pressure techniques by controlling the structure of precursors formed by sol–gel methods.

$\text{YSr}_2\text{Cu}_3\text{O}_y$ superconductor, which can be represented as $\text{CuSr}_2\text{YCu}_2\text{O}_y$, was first synthesized by Okai [1] using a high pressure technique. The superconductor had a superconducting transition temperature T_C onset value of about 60 K. After that, Cu atoms of the CuO chain in the $\text{YSr}_2\text{Cu}_3\text{O}_y$ structure were substituted by high valence elements like Pb [2], Tl [3], Ga [4], and consequently superconductors described as $(\text{Cu}, \text{M})\text{Sr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ were obtained. Miyazaki *et al.* [5] succeeded in synthesizing the new compound $\text{Y}_{2.0}\text{Sr}_{5.0}\text{Cu}_{6.0}\text{C}_{0.9}\text{O}_{16.2}$ containing carbonic ions. However, the compound did not show superconductivity. A superconductor incorporating carbonic ions, $(\text{Y}_{0.5}\text{Ca}_{0.5})_{0.95}\text{Sr}_{2.05}\text{Cu}_{2.4}(\text{CO}_3)_{0.6}\text{O}_y$, was found by Akimitsu *et al.* [6]. It was prepared by repeating solid phase reactions and heating under 10 MPa gas pressure of CO_2 .

We attempted to synthesize $\text{CuSr}_2(\text{Y}, \text{Ca})_2\text{Cu}_3\text{O}_y$ superconductors under mild conditions by using sol–gel methods. During this research, a $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor with a T_C onset of about 50 K, was produced under atmospheric pressure via a sol with the metal composition $\text{Cu}:\text{Sr}:(\text{Y}, \text{Ca}):\text{Cu} = 1:2:2:3$. In this paper, we will report the synthesis of a $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor under atmospheric pressure.

2. Experimental procedure

2.1. Preparation

In order to synthesize $\text{CuSr}_2(\text{Y}, \text{Ca})_2\text{Cu}_3\text{O}_y$ superconductors a sol–gel method was used. The nominal composition of $\text{CuSr}_2\text{Y}_{2-x}\text{Ca}_x\text{Cu}_3\text{O}_y$, x ranging from 0 to 1.3, was examined. $\text{Cu}(\text{OH})_2$ was used as a source of copper. Metal alkoxides of Sr ($\text{O-isoC}_3\text{H}_7$)₂, Ca ($\text{O-isoC}_3\text{H}_7$)₂ and Y($\text{O-isoC}_3\text{H}_7$)₃ were used as sources of the other metal elements. $\text{Cu}(\text{OH})_2$ was dissolved in a mixture of dimethylaminoethylalcohol (DMAE) and isopropyl alcohol (IPA). The metal alkoxides were dissolved in IPA alone according to each composition. The two solutions were mixed, reacted at 60 and 90 °C under refluxing, and then condensed at 90 °C under vacuum to obtain sol and further gel. These processes were carried out in a flowing inert gas or vacuum. Gels were subsequently dried at 200 °C under vacuum. Dried gels were calcined at 800 °C in a mixed gas of $\text{O}_2/\text{N}_2 = 1/4$ in order to form a powder. The calcined powders were compacted to a cuboid of about $3 \times 3 \times 15$ mm³. The rectangular bulk samples were sintered according to controlled heating schedules which consisted of two processes. That is, the samples were heated between 850 to 950 °C in flowing N_2 gas, and subsequently sintered at higher temperatures of 850 to 1050 °C in flowing O_2 gas.

2.2. Characterization

A gel was analysed by Fourier-transform infrared absorption (FTIR) and extended X-ray absorption near edge structure (EXAFS) spectroscopies. Phases formed under each heating condition were identified by powder X-ray diffraction using CuK_α radiation. The structures of some crystals in the sintered samples were investigated in detail by high-resolution

transmission electron microscopy (HRTEM). The chemical composition of the crystals was analysed by energy dispersive X-ray (EDX) spectroscopy. The electric resistance versus temperature characteristics of sintered samples were measured by the standard four-probe d.c. method in which four electrodes were formed by depositing gold to connecting gold wires with a silver paste. Magnetization of the samples was measured with a SQUID magnetometer.

3. Results

In preliminary examinations, $\text{Cu}(\text{OH})_2$ did not dissolve in IPA alone. It also took about half a day to dissolve $\text{Ca}(\text{O-isoC}_3\text{H}_7)_2$ in IPA. The dark blue mixed solutions became viscous with condensing at 90°C , and no precipitates were deposited. A FTIR study indicated that C-N, C-O, NC-H, and M-O (and/or N) bonds (M is thought to be copper) existed in the synthesized sol. Local configuration of elements around copper in the sol was investigated by EXAFS

TABLE I Local configuration of elements around Cu of a precursor (sol)

Neighbouring order	Species	Distance from Cu (nm)	Coordination numbers	Fitting residual (%)
First	O	0.188	2.01	22.9
Second	O	0.256	1.97	12.8
	N	0.259	1.96	14.5
Third	Cu	0.309	1.59	25.5

Note: The values for the third species (Cu) were obtained from a Ba containing sol.

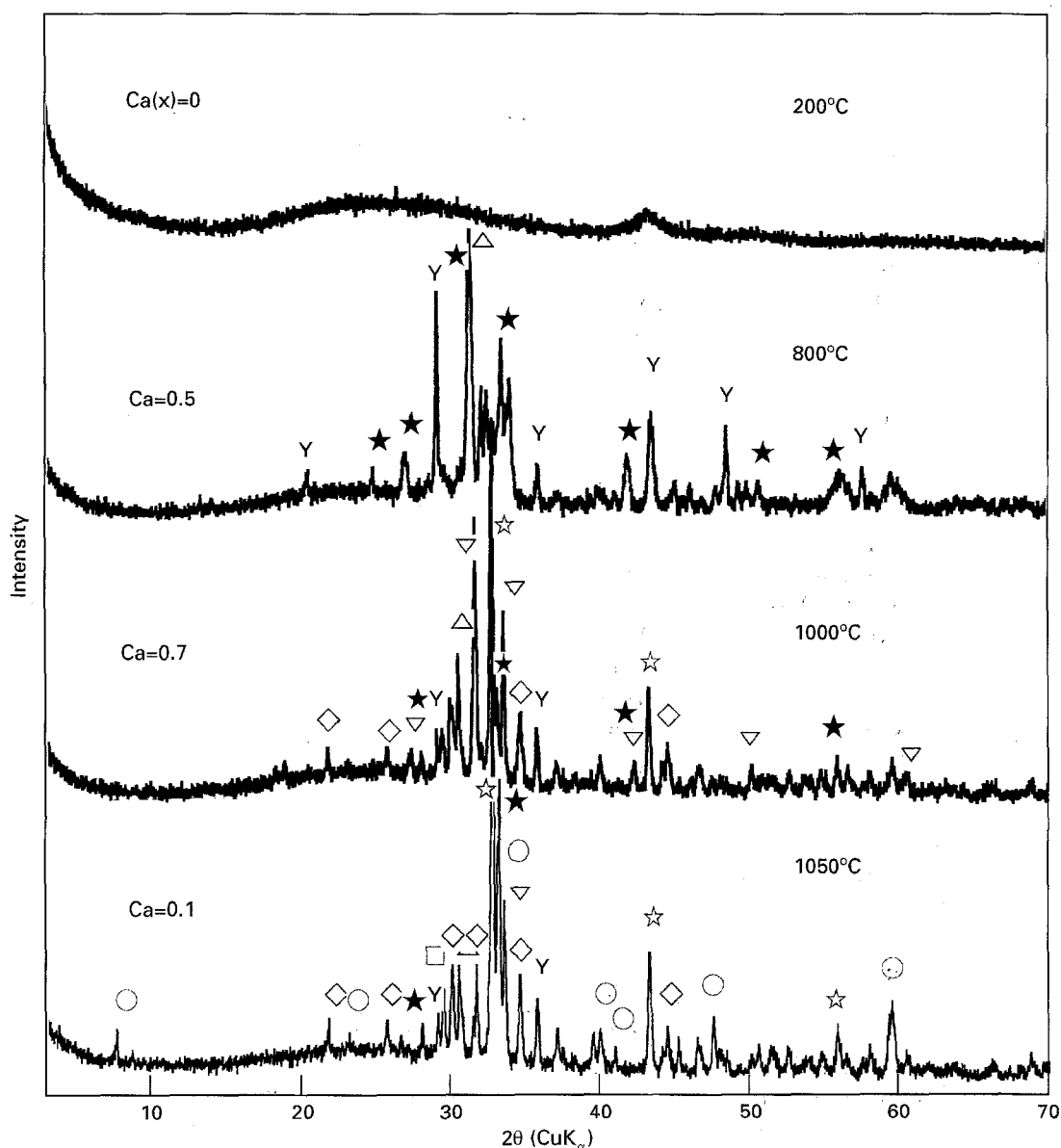


Figure 1 Dependence of the XRD pattern of samples heated at 1050°C for 10 h on the Ca composition. Key: ☆ Sr_2CuO_3 ; ★ $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$; Y Y_2O_3 ; □ SrY_2O_4 ; ◇ $(\text{Sr}, \text{Ca})\text{CuO}_2$; ▽ $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$; △ $\text{Cu}_2\text{Y}_2\text{O}_5$; ○ 123 phase.

spectroscopy. The results obtained are summarized in Table I. The first neighbouring element was oxygen and the distance between O and Cu was 0.188 nm, which is quite close to that of the CuO_2 plane of cuprate superconductors. Oxygen and nitrogen were selected for second neighbouring elements. The distances of second O and N from Cu were 0.256 and 0.259 nm, respectively. These values are similar to the distance between apical O and Cu of the CuO_2 plane of cuprate superconductors. The distance between Cu elements was estimated to be 0.309 nm and corresponded to the third distance. This distance was obtained from the Ba containing sol (Ba-sol) instead of the Sr containing sol (Sr-sol), because the third distance was not clarified for the Sr-sol. However, the distance of the Sr-sol is thought to be equivalent to that of the Ba-sol.

Gels dried at 200 °C were practically amorphous. When the dried gels were calcined at 800 °C, large amounts of $\text{Cu}_2\text{Y}_2\text{O}_5$ and Y_2O_3 were deposited and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ was also seen in every sample. Fig. 1 shows crystalline phases formed in the samples with

various Ca compositions when they were heated at 950 °C for 10 min in flowing N_2 gas and subsequently at 1050 °C for 10 h in flowing O_2 gas. Y_2O_3 decreased in quantity as compared with the 800 °C calcined powder and SrY_2O_4 was formed instead. In samples with the x value (Ca composition) ≤ 0.5 , $\text{Cu}_2\text{Y}_2\text{O}_5$ is the main phase. In samples with $x \geq 0.7$, however, Sr_2CuO_3 grows as the main phase instead of $\text{Cu}_2\text{Y}_2\text{O}_5$. $(\text{Sr}, \text{Ca})\text{CuO}_2$ is also seen and increases with the x value. A phase equivalent to the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_y$, abbreviated to Y-123, is seen only in the sample with $x = 0.7$. Fig. 2 shows crystalline phases formed in a sample with $x = 0.7$ and with increasing temperature. $\text{Cu}_2\text{Y}_2\text{O}_5$, Y_2O_3 and $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ are formed at 800 °C. $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ is reduced markedly, and instead $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$ is formed on heating at 1000 °C. When the temperature is raised by only 50 °C, $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$ practically disappears and a phase similar to Y-123 is formed. This crystal was analysed using HRTEM. A typical example of the electron diffraction patterns of the crystals is shown in Fig. 3. Every diffraction pattern of the crystals, which

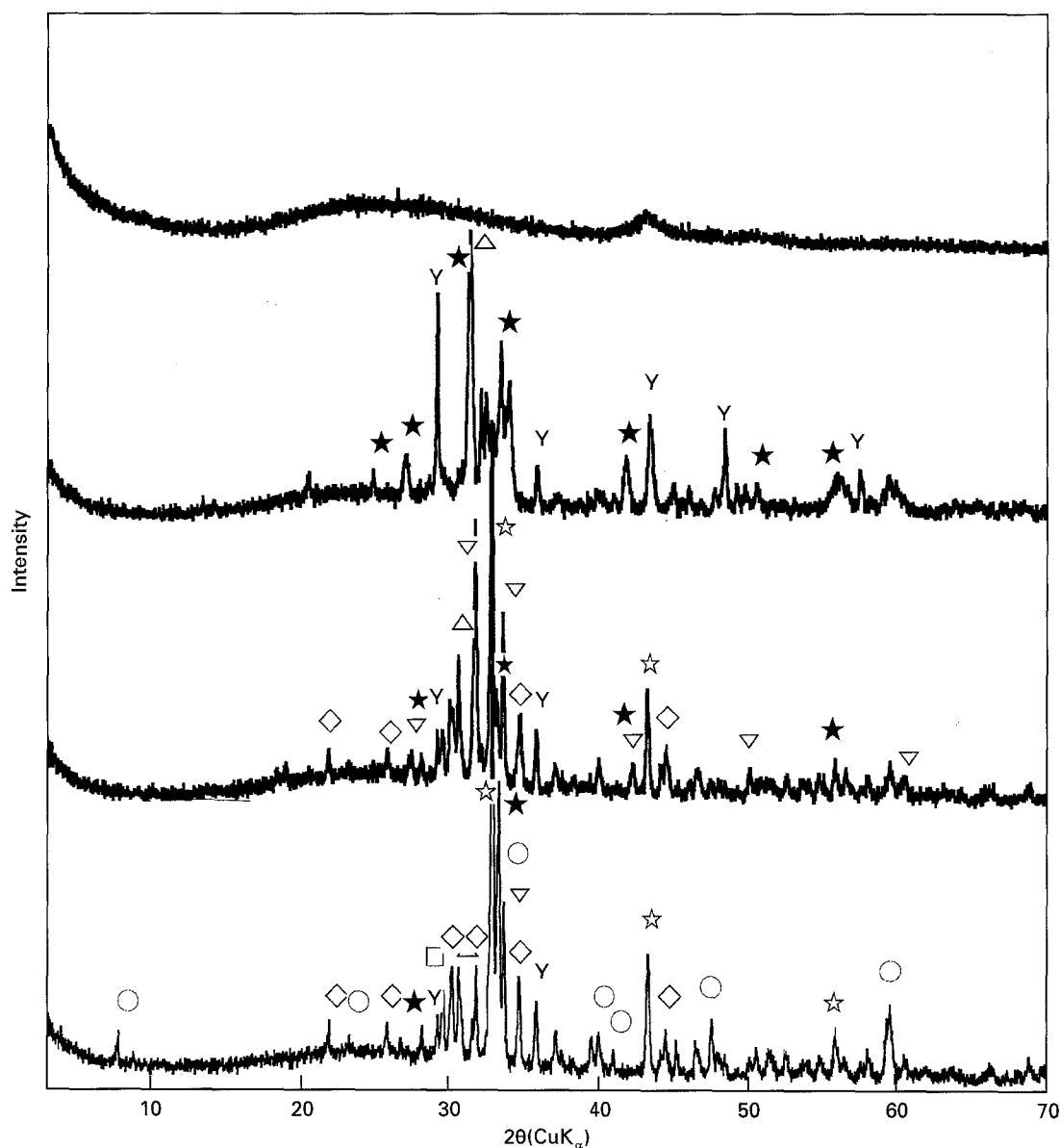


Figure 2 Dependence of the XRD pattern of samples with the x value (Ca composition) of 0.7 on heating temperatures. Key: Δ $\text{Cu}_2\text{Y}_2\text{O}_5$; Y Y_2O_3 ; \star $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$; ∇ $\text{Ca}_2\text{Cu}_7\text{Sr}_3\text{O}_x$; \star Sr_2CuO_3 ; \square SrY_2O_4 ; \diamond $(\text{Sr}, \text{Ca})\text{CuO}_2$; \circ 123 super.

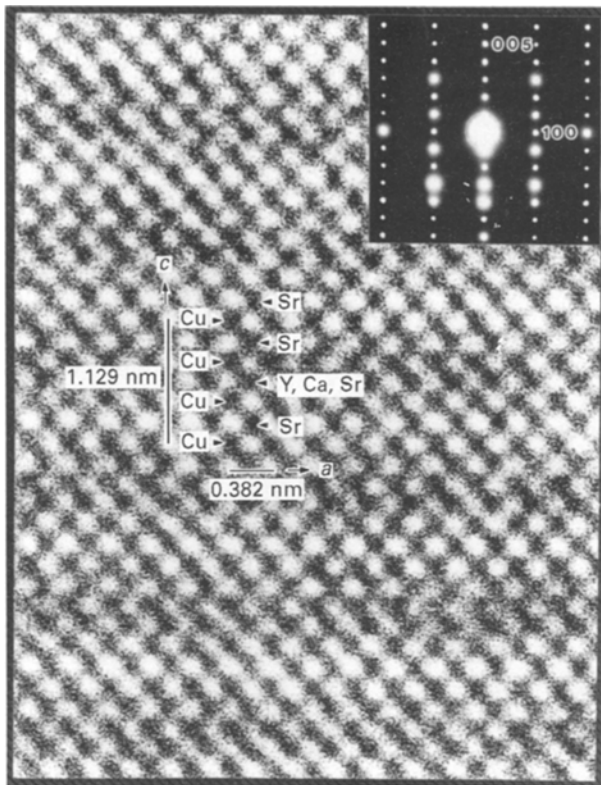


Figure 3 An electron diffraction pattern and a HRTEM image of $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ crystal projected along the direction perpendicular to the c -axis. These are similar to those of the tetragonal $\text{YBa}_2\text{Cu}_3\text{O}_y$ structure.

was projected along the direction perpendicular to c , namely, a or b -direction, was the same. No additional diffraction spots indicating the existence of a superstructure were observed. Therefore, this crystal was presumed to have a tetragonal symmetry in which a is 0.382 nm and c is 1.129 nm. This c value is slightly larger than that of the superconductor synthesized by Akimitsu *et al.* [6]. Fig. 3 also shows a HRTEM image of the crystal projected along the same direction. The contrast of the image is similar to that from Y-123. The results of composition analysis for the crystals by EDX spectroscopy is given in Table II. Average metal composition of the crystals is estimated to be $\text{Y}/\text{Ca}/\text{Sr}/\text{Cu} = 0.9/0.1/2.0/2.4$.

Fig. 4 shows the temperature dependence of d.c. susceptibility of samples heated at 950 °C in flowing N_2 gas and subsequently at 1050 °C for 10 h in flowing O_2 gas. A sample with $x = 0$ and a sample with $x = 1.0$ shows paramagnetic and antiferromagnetic

TABLE II Chemical composition of the 1 2 1 2 crystals

	(Atomic ratios)			
	Cu	Sr	Ca	Y
	43.87	38.07	2.00	16.06
	43.70	37.86	2.01	16.44
	43.99	37.33	1.83	16.85
	43.37	38.04	2.45	16.15
Average	43.62	38.06	2.23	16.11

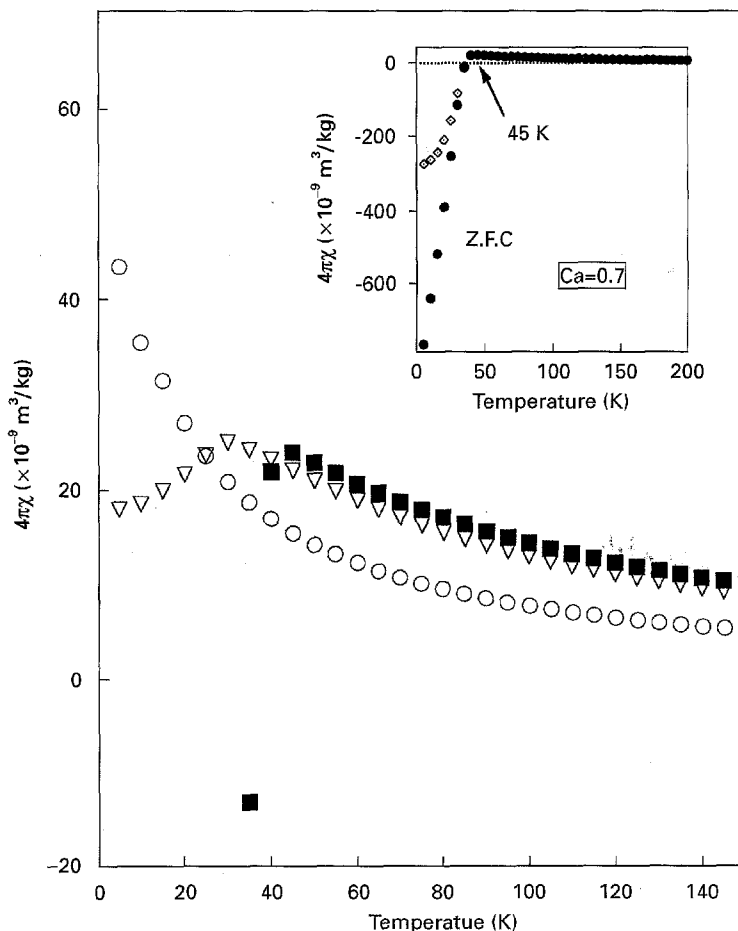


Figure 4. Temperature dependence of magnetic susceptibility of samples with various Ca compositions (x values), which were heated at 1050 °C for 10 h. Key: \circ $\text{Ca}(x) = 0$; ∇ $\text{Ca} = 1.0$; \blacksquare $\text{Ca} = 0.7$. Inset: key: \diamond F.C.; \bullet Z.F.C.

characteristics, respectively. Only the sample with $x = 0.7$ shows diamagnetism from 45 K. The small figure inserted in Fig. 4 shows a susceptibility versus temperature curve with the $x = 0.7$ sample, which was measured under both zero field and field cooling conditions in a field of 7958 Am^{-1} . Temperature dependence of electric resistance of a sample with $x = 0.7$ is shown in Fig. 5. Resistance increases gradually from around 150 K and drops drastically at 51 K to zero. Both magnetization and resistance measurements indicate that the sintered sample with $x = 0.7$, $\text{CuSr}_2\text{Y}_{1.3}\text{Ca}_{0.7}\text{Cu}_3\text{O}_y$, includes a superconductor.

4. Discussion

The structure of the synthesized sol, which was assumed from the results of FTIR and EXAFS studies, is

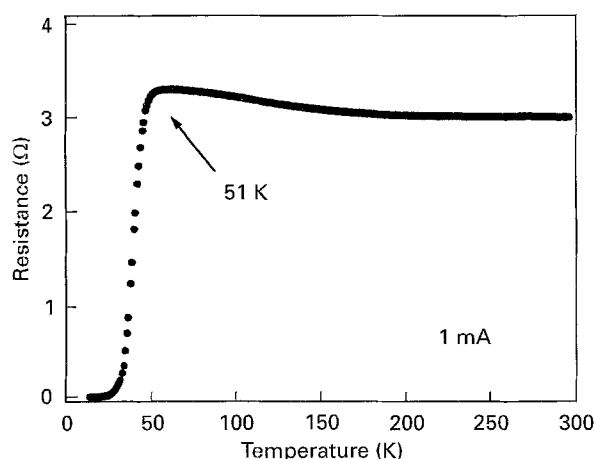


Figure 5 Electric resistance-temperature curve of a sample with an x value of 0.7.

illustrated in Fig. 6. In this figure, Cu is assumed to be surrounded by six ligands of O and N, although the possibility of four ligands cannot be excluded. Cu is thought to be connected with a neighbouring Cu via O, because the distance of Cu-Cu should be less than that estimated from the EXAFS study, 0.309 nm, if Cu atoms bond directly to each other like copper acetate. The resulting fact that alkali earth elements, Sr and Ca (or Ba), were not detected as a neighbouring element suggests that the alkali elements are away from Cu.

$\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$, which consists of a distorted double Cu-O chain, is assumed to be induced without difficulty from the synthesized gel (or sol), because a bent bond of Cu-O-Cu already existed in the gel. $\text{Cu}_2\text{Y}_2\text{O}_5$ which was formed in an early stage of the heating processes is thought to incorporate a slight amount of Ca. Therefore, $(\text{Sr}, \text{Ca})_2\text{CuO}_3$ and $(\text{Sr}, \text{Ca})\text{CuO}_2$, which have the Cu-O chains, increased as the Ca composition was above 0.5. $(\text{Sr}, \text{Ca})_2\text{CuO}_3$ and $(\text{Sr}, \text{Ca})\text{CuO}_2$ are thought to be more stable than $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ at temperatures higher than 1000°C . It is conjectured that $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ reacts with $\text{Cu}_2\text{Y}_2\text{O}_5$ at about 1000°C to form a phase similar to Y-123 via $(\text{Ca}, \text{Y})_2\text{Cu}_7\text{Sr}_3\text{O}_x$. The appropriate ratio of $\text{Sr}_{14}\text{Cu}_{24}\text{O}_{41}$ and $\text{Cu}_2\text{Y}_2\text{O}_5$ for forming this phase is assumed to occur under the limited condition of a Ca composition of 0.7.

It is considered from the results obtained that the sintered sample with the nominal composition of $\text{CuSr}_2\text{Y}_{1.3}\text{Ca}_{0.7}\text{Cu}_3\text{O}_y$ includes a tetragonal $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor similar to Y-123. However, the possibility of incorporation of carbons into the Cu sites of the Cu-O chain cannot be completely ruled out, because a Cu deficiency was indicated by the EDX analysis.

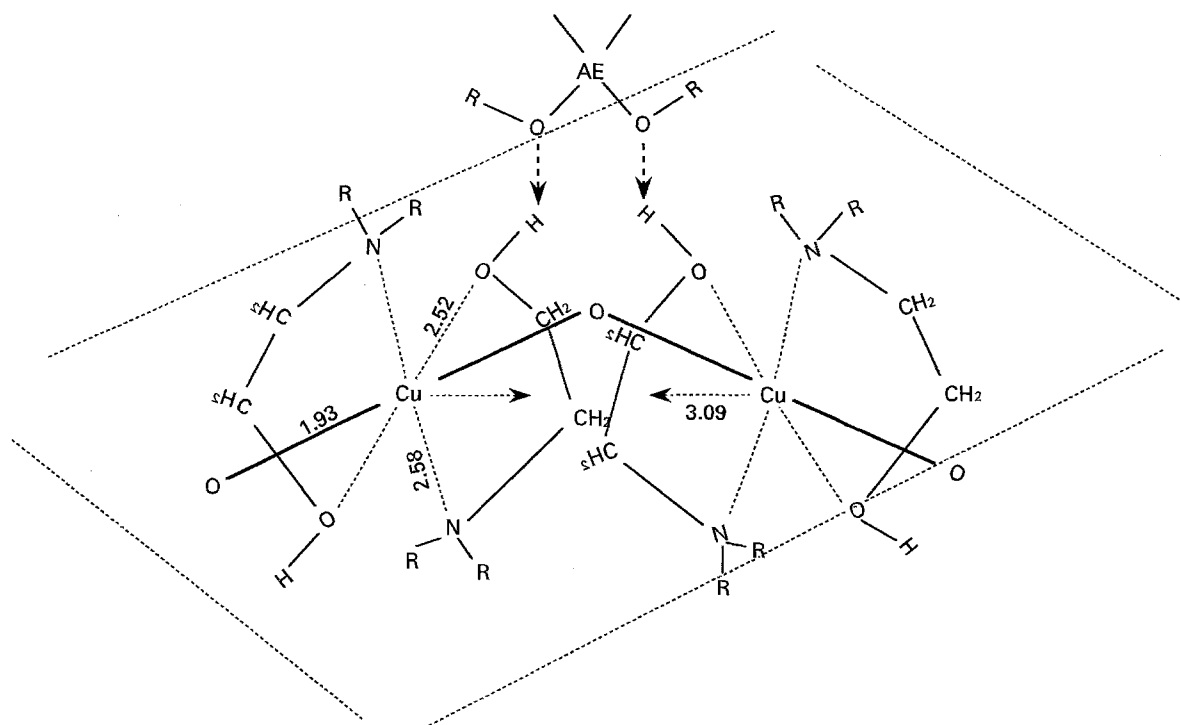


Figure 6 Illustration of the structure presumed for a synthesized sol.

5. Conclusions

A $\text{CuSr}_2(\text{Y}, \text{Ca})\text{Cu}_2\text{O}_y$ superconductor has been synthesized from a sol, the nominal metal composition of which was $\text{Sr}/\text{Y}/\text{Ca}/\text{Cu} = 2/1.3/0.7/4$. Superconductivity of this phase was found by both diamagnetism below 45 K and a drastic decrease of electric resistance to zero from 51 K. The superconductive crystal had a tetragonal symmetry in which a was 0.382 nm and c was 1.129 nm. The chemical composition analysed by EDX spectroscopy, namely, $\text{Y}/\text{Ca}/\text{Sr}/\text{Cu} = 0.9/0.1/2.0/2.4$, implies that some of the Cu atoms of the Cu–O chain might be substituted by carbons. It has been demonstrated that contriving the structure of precursors by sol–gel methods is useful to synthesize high pressure phase cuprate superconductors.

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