

Superconducting Phase Formation and Properties in the Bi-Sr-Ca-Cu-O System

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Bi-Sr-Ca-Cu-O 계에서 초전도체 상형성 및 특성

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초 록 Bi-Sr-Ca-Cu-O계에서 상형성에 관해 연구하였다. 임계온도가 80K인 초전도체는 Bi : Sr : Ca : Cu의 몰비율이 2 : 2 : 1 : 2의 성분으로부터 solid state synthesis의 방법으로 합성하였다. 이때 이상에 대한 x-ray diffraction pattern은 모두 색인하였다. 2 : 2 : 1 : 2를 기본으로 한 solid solution의 형성을 $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+y}\text{Cu}_2\text{O}_{8+z}$ 으로 단일상(single phase)을 형성하고 있으며, 이때 x와 y의 범위는 $0 < x < 0.3$ 그리고 $0 < y < 0.3$ 이다. 높은 임계온도의 초전도체상(2223)은 $\text{BiSrCaCu}_2\text{O}_8$ 의 조성식으로부터 거의 순수한 상을 합성하였다. 이 상에 대한 합성조건은 특별히 구조상의 긴영역의 확산과 아울러 매우 좁은 온도영역의 안정성때문에 매우 까다롭다. 이 실험의 결과 105K초전도체상은 오직 Cu의 양이 많은 조성으로부터만 형성되었고, 105K로 전이시 긴 저항꼬리가 있는 점으로 보아 grain boundaries에서의 불순물로 추정된다.

Abstract Phase formation in the Bi-Sr-Ca-Cu-O System has been investigated. The 80K superconducting phase(2212) was successfully prepared with nominal composition 2 : 2 : 1 : 2 (Bi-Sr-Ca-Cu) using solid state synthesis. The x-ray powder diffraction pattern was fully indexed. An area of 2212 based solid solution formation given by the formula $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+y}\text{Cu}_2\text{O}_{8+z}$, where $0 < x < 0.3$ and $0 < y < 0.3$, was obtained as a single phase. The high-Tc superconducting phase(2223) was obtained almost phase pure from the nominal composition of $\text{BiSrCaCu}_2\text{O}_8$. The conditions for the preparation of the high-Tc phase were very critical, because of the long range diffusion needed and especially its narrow temperature stability domain. From the results of this work, the 105K superconducting phase was only produced from Cu-rich compositions : however, a superconduction transition at 105K slways contains a long resistance tail, perhaps associated with the presence of small amounts of impurities at the grain boundaries.

1. Introduction

Since the discovery of superconductivity in the Bi-Sr-Ca-Su-O system by Maeda et al¹⁾, intensive studies of phase formation and superconducting properties have been carried out for compositions close to the ideal $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ (80K, 2212) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (110K, 2223) phase compositions. It has proved difficult to

synthesize single phase samples of the 2212 and 2223 phases with the ideal starting compositions, in spite of much effort by many investigators. Escudero et al²⁾. Suggested that this difficulty in preparing a single phase sample is related to the inherent instability of the structure, partially due to the long C direction compared to that of A and B, which is reflected in the high degree of disorder between the differ-

ent atomic layers of CuO, Sr-O, Bi-O and Ca-O. Moreover, the solid-state reaction is accomplished at temperatures quite close to the melting point of the compound, where high ionic mobility is expected and therefore a high degree of disorder occurs in the different layers.

Several groups succeeded in preparing the 80K superconducting phase³⁻⁵⁾, soon after the original discovery of the 80K phase by Maeda et al¹⁾. These early experiments indicated that the approximate composition of the 80K phase was $\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_x$, with a broad range of mutual solubility between Sr and Ca. Others^{6,7)} have investigated the composition of the 2212 phase by energy dispersive x-ray analysis (EDX) of single crystal samples, grown by flux or melt-quenching techniques. The results showed that the crystals grown by these methods have the Bi-excess compositions $\text{Bi}_{2-1-2}\text{Sr}_2\text{CaCu}_2\text{O}_x$. Several other reports⁸⁻¹¹⁾ on the identifications of 2212 phase indicated that Ca and Sr form a solid solution $\text{Si}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_x$ in this material.

Chippindale et al¹²⁾ identified two superconducting phases in samples with initial mole ratios $\text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 1 : 1 : 1 : 2$ and $1 : 1 : 1 : 1$ and determined their stoichiometries using energy dispersive x-ray analysis (EDX) as $\text{Bi}_2(\text{Sr}, \text{Ca})_{1.5}\text{CuO}$, and $\text{Bi}_2(\text{Sr}, \text{Ca})_{2.66}\text{Cu}_2\text{O}$. This result indicated that the true compositions of the 80K superconducting phases in the Bi-Sr-Ca-Cu-O system are Sr deficient. Nagano et al.¹³⁾ investigated Sr-deficiency in the 2212 phase showing that about 10% of the Sr^{2+} ions are vacant for $\text{Bi}_2\text{Sr}_{2-x}\text{CaCu}_2\text{O}$. Recently, Karbarz et al¹⁴⁾ investigated phase formation from the nominal composition $\text{Bi}_2\text{Sr}_{(2+x)}\text{CaCu}_2\text{O}$, for $0 < x < 0.5$. The results showed that a Sr deficient stoichiometry exhibited the highest phase purity. A superconducting phase having composition $\text{Bi}_4(\text{Sr}, \text{Ca})_6\text{Cu}_4\text{O}_{16+x}$ was isolated by Tarascon et al³⁾ and the crystal structure of the 2212 phase determined; however, in the bulk material, a mixture of two phase was always

detected. Their results indicated that a solid solution exists over the $\text{Bi}_2\text{Sr}_{(3+x)/2}\text{Ca}_{(3-x)/2}\text{Cu}_2\text{O}_y$ composition range $-0.5 < x < +0.5$.

The 110K phase, however, has not been successfully isolated from the ideal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. Careful temperature control is required to form the high-Tc phase which is generally found as an intergrowth between the 2201 and 2212 phase, as shown by transmission electron microscopy (TEM)^{6,15)}. Wada et al⁶⁾ obtained a 110K transition after transformation of the low-Tc phase, $\text{Bi}_2(\text{Sr}, \text{Ca})_{3-x}\text{Cu}_2\text{O}_y$ through long time sintering, 60 hours, at 860-870°C in air. Recently, Luo et al.¹⁷⁾ reported changes in the structure of $\text{Bi}_4\text{Sr}_3\text{Ca}_3\text{Cu}_4\text{O}_{16+x}$ (4334) on annealing close its melting point, leading to partial formation of the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10+x}$ (2223) phase, as identified by x-ray diffraction (XRD) and confirmed by electrical resistivity measurements. This result is consistent with the Tarascon et al.³⁾ who reported that an heating single phase 4334, initially having Tc 85K, near its melting point, produce its sharp resistivity drop at 110K. Luo et al observed regions transformed to the 2223 phase, bounded by an amorphous phase using TEM. The result, however, showed that the composite microstructure contains 4334 and 2234 with a majority 2223 phase. The mechanism and phase relations in the Bi-Sr-Ca-Cu-O system are still not fully understood.

The preparation condition of a 110K phase have been studied in terms of the heat treatments and various starting compositions by several authors¹⁶⁻²¹⁾. Results showed a sharp resistance drop near 110K. This long resistivity trail was present in all the samples exhibiting the 110K transition¹⁶⁻²¹⁾. Until now, the 2223 phase has essentially only been obtained in a nearly pure form with substitution of Pb^{2,22,23)}. To determine the intrinsic properties of the newly discovered high-Tc superconductors, Pb-free single phase samples of the 110K phase are necessary.

In this work, 2212 and 2223 phase forma-

Table 1. Weight Change Studies During Reaction

Sample	Treatments	Cumulative weight loss(%)	Standard Deviation
Powder	600°C, 24H	6.01	
	700°C, 24H	9.31	
	800°C, 24H	12.58	
Pellet	800°C, 86H	12.77	0.03
	880°C, 168H	12.77	0.03

tion in the Bi-Sr-Ca-Cu-O system has been systematically investigated. As it was suspected that the oxygen content varies by changing the ratio of Sr and Ca in the solid solution, the effect of also changing oxygen content on the superconducting properties was investigated. Different annealing conditions were used to control the oxygen content of compositions in the solid solution region. The dependence of lattice parameters and critical temperatures upon solid solution composition were investigated.

In order to investigate 2223 phase formation, various nominal compositions were prepared and phase formation examined using x-ray powder diffraction(XRD), energy dispersive x-ray analysis(EDX) and electrical resistivity measurements.

2. Bi₂Sr₂CaCu₂O_x(2212) phase

2212 phase formation

Weight loss studies

Single phase, polycrystalline Bi₂Sr₂CaCu₂O_x samples were prepared using solid synthesis techniques. Completeness of reaction and phase purity of the samples was checked by x-ray powder diffraction. Weight changes studies were carried out to ensure that no loss of reactants, apart from CO₂, occurred during either the reaction or subsequent annealing treatments. Theoretical weight loss for 2SrCO₃+CaCO₃+Bi₂O₃+2CuO → Bi₂Sr₂CaCu₂O_x=12.94%. The difference between observed loss, 12.77% and calculated, 12.94% may be attributed to the excess oxygen retained in the sample since x≈0.17 after heating at 820°C. For formation of Bi₂Sr₂CaCu₂O_{3.17}, the expected weight

loss ((0.1%) during reaction and in particular, confirmed that the Bi, Sr, Ca and Cu content of the product was the same as that of the starting mixture. Consequently, any deficiency of Bi, which is the most volatile component, in the product must be less than 0.2mol % Bi₂O₃.

Solid solution formation

Solid solution formation based on the 2212 phase has been investigated in the CaO-SrO-BiCuO₂ system. Samples with the starting compositions, Bi₂Sr_{2-x}CaCu₂O_x(x=0.1-0.5), and other compositions close to Bi₂Sr₂CaCu₂O_x(2212 phase), as shown in figure 1(b), were prepared by solid state synthesis. First, the ground powder was reacted at 700-800°C for 1-2 days. Second, the powder was pressed into pellets and fired at temperatures in the range 800-880°C. Samples reacted at these temperatures, as a powder, were always multiphase, containing the low-T_c 2201 phase and CuO. Pelletisation greatly assisted in the production of phase formation by pressing into pellets may be due to densification and easy nucleation compared to that of powder.

Single phase samples were found for both Bi₂Sr_{2-x}CaCu₂O_x(Sr deficient) and Bi₂Sr_{2-x}Ca_{1+x}Cu₂O_x(Ca for Sr substitution) solid solutions for x=0.1, 0.2 and 0.4. The composition of the samples, the minimum time of heat treatment for single phase formation (850-880°C) and resultant are listed in table. 2.

The times required for single phase formation for the Sr deficient compositions were significantly less than for pure 2212 or Ca for Sr deficient substitution. The secondary phases which appeared outwith the solid solution re-

Table 2. Sample Preparation and Characteristics.

Nominal composition	Minimum time(days) (850-880°C)	Phase present after reaction	Others
$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$	6-7	single	2212 phase
$\text{Bi}_2\text{Sr}_{1.9}\text{CaCu}_2\text{O}_x$	5	single	Sr deficient
$\text{Bi}_2\text{Sr}_{1.8}\text{CaCu}_2\text{O}_x$	3	single	composition
$\text{Bi}_2\text{Sr}_{1.7}\text{CaCu}_2\text{O}_x$	3	single	
$\text{Bi}_2\text{Sr}_{1.6}\text{CaCu}_2\text{O}_x$	5	multi-phase	
$\text{Bi}_2\text{Sr}_{1.5}\text{Ca}_{1.1}\text{Cu}_2\text{O}_x$	5	single	Ca for Sr
$\text{Bi}_2\text{Sr}_{1.4}\text{Ca}_{1.2}\text{Cu}_2\text{O}_x$	5	single	substitutional
$\text{Bi}_2\text{Sr}_{1.3}\text{Ca}_{1.3}\text{Cu}_2\text{O}_x$	5	single	composition
$\text{Bi}_2\text{Sr}_{1.6}\text{Ca}_{1.4}\text{Cu}_2\text{O}_x$	5	multi-phase	

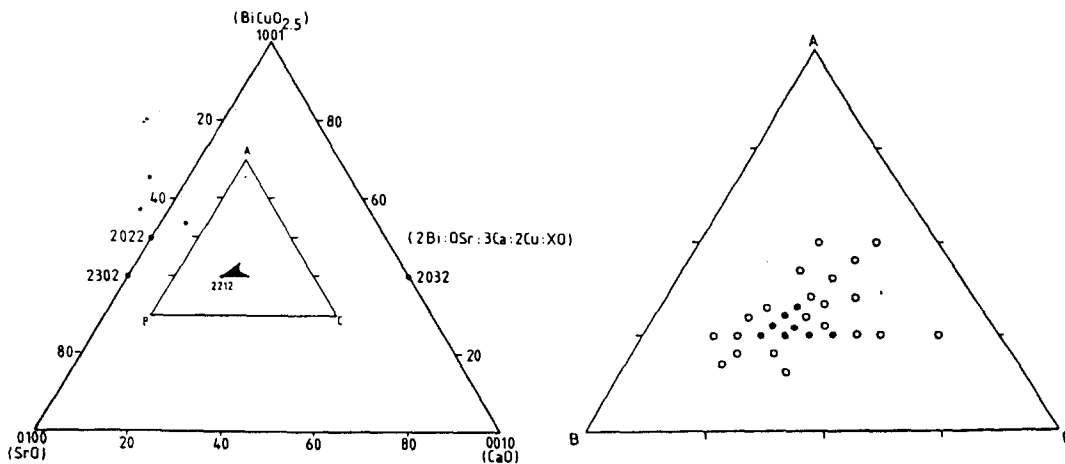


Fig. 1. (a) 2212 based ksolid solution region in the SrO-CaO-"BiCuO_{2.5}" system. (b) Expanded view of triangle (A, B, C) shown in (a). Solid circles(●) indicate the presence of single phase compositions. Open circles(○) indicate two or more phases resultin from heat treatment.

gion(x)0.3) were mainly the $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (2201) phase with some CuO. Figure 1. shows the area of solid solution formation in the CaO-SrO-"BiCuO_{2.5}" system. All of the single phase solid solutions were found in a plane where the Bi and Cu andtents were equal. No single phase samples were found along the join $\text{Bi}_2\text{Sr}_3\text{Cu}_2\text{O}_x$ (2302) to $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212).

Solid solution formation out of the CaO-SrO-"BiCuO_{2.5}" plane was also investigated. Little evidence for single phase solid solution formation was found. In order to complete the study of solid solution phase formation in the Bi-Sr-Ca-Cu-O system, compositions out of the CaO-SrO-"BiCuO_{2.5}"plane require further investi-

gation

Characterization of 2212 phase based solid solution

Lattice parameter measurements

The existence of a solid solution can be shown unambiguously by measuring the lattice parameters as a function of composition x. The A and C lattice parameters for the solid solutions $\text{Bi}_2\text{Sr}_{2-x}\text{CaCu}_2\text{O}_x$ and $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_x$ and plotted against composition x in figure 2 and 3. As shown, for both Sr deficient and Ca for Si substitutional solid solutions, the lattice parameter A was constant within error but the lattice parameter along the C axis monotonically decreases as the Ca content in

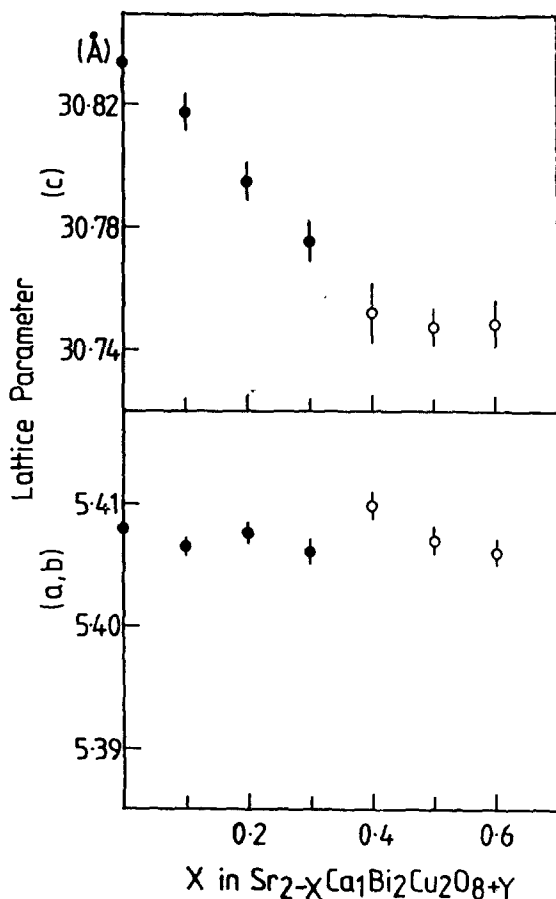


Fig. 2. Lattice parameters of BiSrCaCuO as a function of x. Solid circles(●) indicate the presence of single phase compositions. Open circles(○) indicate two or more phases.

creases because of the larger Sr ionic radius compared to that of Ca, as suggested by Grader et al⁵⁾. In the Sr-deficient solid solution the C lattice parameters also decrease as the Sr content decreases, probably because of the removal of Sr(and O) atoms from the unit cell. The decrease of the C lattice parameter with x as shown in figures 2, and 3, is in accordance with the behaviour predicted by Vegard's rule²⁴⁾.

Critical temperature measurement

The Variation of critical temperature, T_c , within the solid solution region was investigated. Samples were either annealed at 880°C in air and quenched to room temperature or at 400°C in N_2 to control oxygen content and investigation T_c -oxygen content correlations as

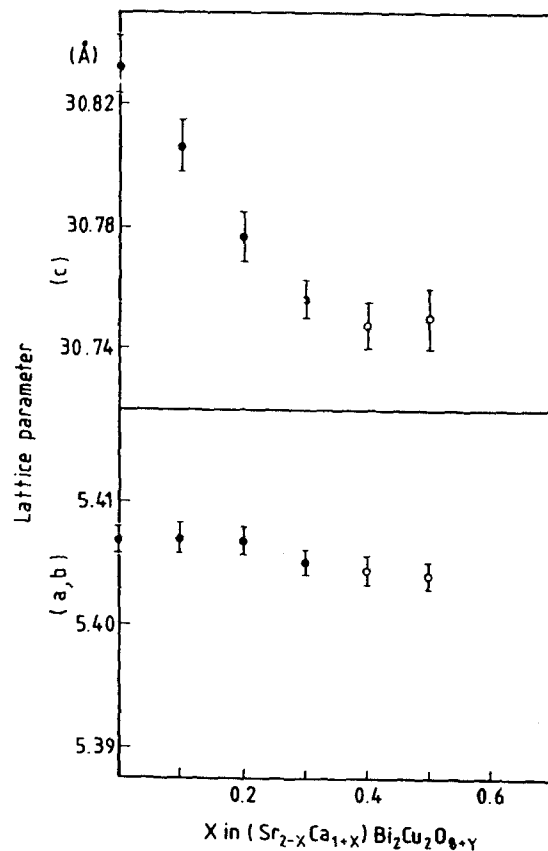


Fig. 3. Lattice parameters of BiSrCaCuO as a function of x. Solid circles (●) indicate the presence of single phase compositions. Open circles (○) indicate two or more phases.

a function of composition, x, for both solid solution regions. Figure 4 and 5 show the resistnace transition as a function of composition x in the Sr deficient and Ca for Sr substitutional solid solution, respectively. Higher T_s were obtained for each solid solution from the samples which were annealed at 400°C in N_2 than those annealed at 880°C in air. For the sample annealed at 880°C in both $Bi_2Sr_{2-x}CaCu_2O_y$ and $Bi_2Sr_{2-x}Ca_{1+x}Cu_2O_y$, the critical temperatures were quite similar to each other. For the samples annealed at 400°C in N_2 , T_c decreased slightly on going from x=0 to 0.3 in both systems.

Oxygen content measurement

The oxygen content of the Sr deficient samples($Bi_2Sr_{2-x}CaCu_2O_y$) and Ca for Sr substitutional($Bi_2Sr_{2-x}Ca_{1+x}Cu_2O_y$) solid solution which

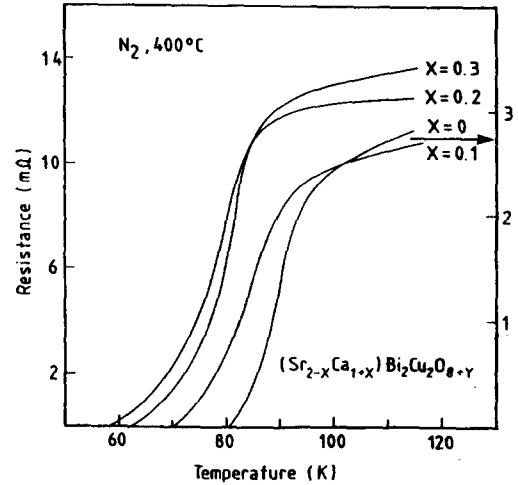
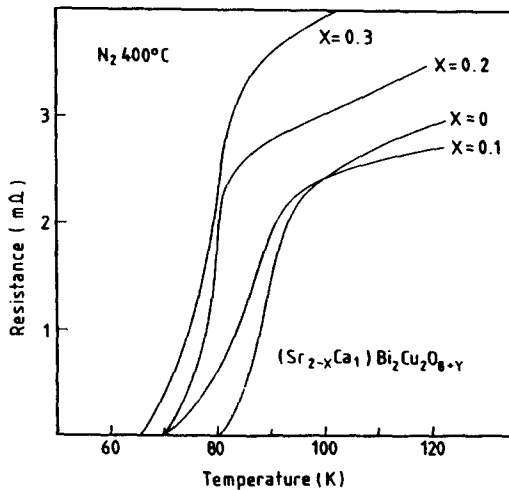
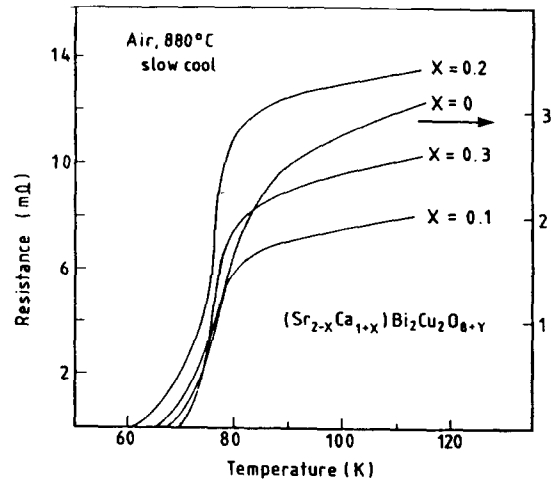
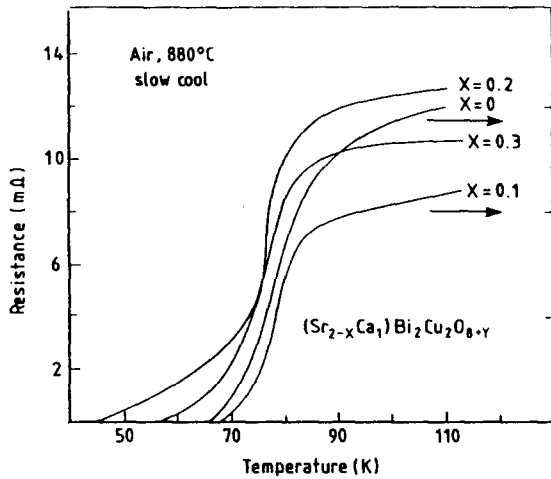


Fig. 4. Resistance versus temperature curves of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_y$.

Fig. 5. Resistance versus temperature curves of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_y$.

had been annealed at 880°C in air, were determined by citrate iodometry method. The oxygen content was calculated using the analysed mean valence value of copper with the charge neutralisation condition, in which formal valence values were assumed, i.e., Bi^3 , Ca^{+2} , Sr^{+2} . Figure 6 shows how the oxygen content and the copper valence change with extent of substitution for both solid solution mechanisms. The total oxygen content, y , in the $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_y$ solid solution was constant in the solid solution region ($x < 0.3$); however, the total oxygen content, y in the $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_y$ compo-

sition decreased linearly on going from $x=0$ to 0.3. The copper valence value in the Sr deficient solid solutions, $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_y$, showed a small, but significant decrease, on going from $x=0$ to 0.3.

Discussion

The oxygen content and copper valence for the Sr-deficient compositions were different from the values predicted by Cheetham et al.²⁵⁾ (figure 6). Cheetham et al proposed that the oxidation of Cu^{2+} in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_8$ is controlled by depleting the Sr content according to the general formula $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_x\text{Cu}_2\text{O}_8$ in which

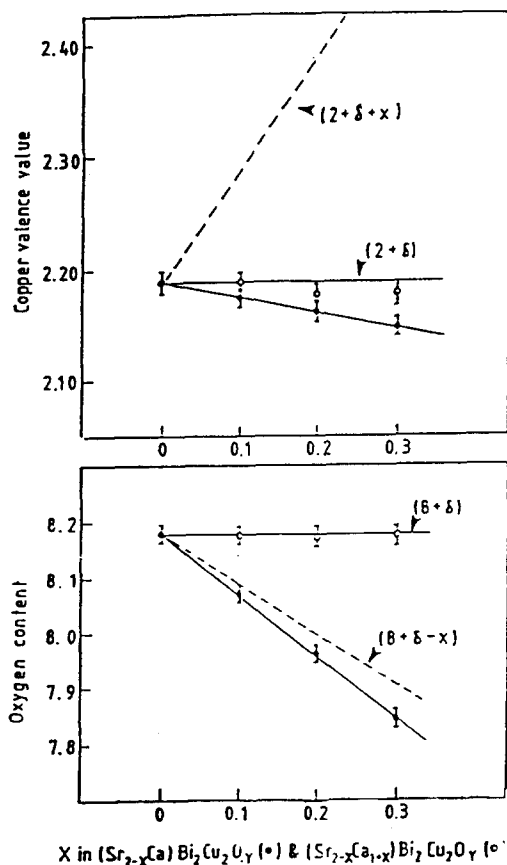


Fig. 6. Oxygen content in the solid solution region. Oxygen content calculated from formal values, Bi, Ca, Sr, Cu and additional oxygen as determined by citrate idometry.

Sr deficiency is charge-compensated by the creation of electron holes in the CuO_2 layer, i.e. $\text{Cu}^{2+} \rightarrow \text{Cu}^{3+}$. This is contrast to the systems $(\text{La}_{2-x}\text{Ba}_x)\text{CuO}_y$ and $\text{YBa}_2\text{Cu}_3\text{O}_x$ in which the copper oxidation state is determined by substitutional defects and oxygen defect, respectively. The difference between the ideal(Cheetham et al.) and measured (this work) values are shown in table. 3.

If Cheentham et al's suggestion was correct, then the copper valence for the Sr deficient solid solutions would increase almost linearly with x, dashed line in figure 6 ; instead there is a slight decrease in the average Cu valence. It is evident that an oxgen is removed from the unit cell for every Sr that is removed, table

Table 3. The Change in Copper Valence Per Additional Sr in $\text{Bi}_2\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$.

This work	Cheetham et al.
$\text{Sr}^{2+} \rightarrow \text{VSr}$	$\text{Sr}^{2+} \rightarrow \text{VSr}$
$(1+y)\text{O}^{2-} \rightarrow \text{VO}$	$(1-x)\text{O}^{2-} \rightarrow \text{VO}$
$(y)2\text{Cu}^{3+} \rightarrow 2\text{Cu}^{2+}$	$(x)2\text{Cu}^{2+} \rightarrow 2\text{Cu}^{3+}$
$y \ll 1$	$0 \ll x \ll 1$

♣ V_{Sr} and V_{O} represent the vacancies of Sr and O atoms in the stoichiometric 2212 phase.

3 first column. Indeed, removal of Sr destabilishes the oxidation environment of the Cu and so leads to a slight decrease in Cu oxidation state.

Moto et al.²⁶⁾ reported that the T_c of $\text{Bi}_2\text{Sr}_{2-x}\text{Ca}_{1+x}\text{Cu}_2\text{O}_y$ ($0 \ll x \ll 1.0$) depends upon heat treatment and composition. Critical temperature, T_c , was measured for samples which were either rapidly quenched into liquid nitrogen or slowly cooled in the furnace to room temperature. The results showed that T_c decreased on going from $x=0$ to 1.0 for the rapid quenched samples, but T_c was almost same for the furnace cooled samples. They²⁶⁾ suggested that the dependence of the critical temperatures upon composition of the solid solutions could be attributed to the changes in the oxygen content caused by changing the Sr/Ca ratio as reported by Niu et al.⁹⁾, and the presence of an optimum hole concentration for the superconductivity as in the pure 2212 phase. Moto et al also suggested an alternative explanation, that the change in structure caused by Sr/Ca substitution affects puckering of CuO_2 planes or alters the distance between the CuO_2 planes, which is expected to directly influence the band structure and the density of states of the fermi energy.

In this report, the measured oxygen content in the Ca for Sr substitutionalnsolid solution region was constant within error, whereas the oxygen content monotonically decreases in the Sr deficient solid solution region. As T_c was observed to change with degree of substitution for both solid solution regions, it appears that

T_c is influenced by other factors as well as oxygen content, for instance structural distortions, induced disorder or band structure changes as suggested by Moto et al.

3. $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223) phase

High- T_c (110K) superconducting phase formation

Heat treatment

Samples with nominal compositions of 1 : 1 : 1 : 2, 2 : 2 : 2 : 3, 3 : 5 : 4 : 3 : 3, 4 : 4 : 3 : 3, and 2 : 1 : 8 : 2 : 3 (Bi : Sr : Ca : Cu) were mixed and reacted in air in the temperature range 800–850°C for 24–48 hours with a few intermediate grindings. The specimens of the calcined black powder were examined by x-ray powder diffraction. After this firing sequence, all the compositions showed a mixture of two phases (2201 and 2212) with very small amounts of 2223 phase in some samples. After grinding and pelleting, they were reacted in air under various heating regimes to investigate phase formation of the high- T_c phase.

Heat treatments were carried out in air in the temperature ranges $T < 870^\circ\text{C}$, $875 < T < 885^\circ\text{C}$, and $T > 890^\circ\text{C}$ for between 3 days and 30 days. For some of the samples, i.e., 2224, treated at temperatures below 870°C, two superconducting phases with transitions at around 80K and 105K were detected from resistivity measurements. X-ray powder diffraction showed the coexistence of two superconducting phases with small amounts of the same temperature did not increase the volume fraction of the high- T_c phase. When the sintering tempera-

ture was increased, i.e., to $880 \pm 5^\circ\text{C}$, the high T_c phase was formed preferentially only for the nominal composition of $\text{BiSrCaCu}_3\text{O}_x$. In this temperature range, slight melting or softening of the surface of the pellet was sometimes noticed depending patterns showed only the high- T_c phase without evidence of any extra phases. Energy dispersive x-ray analysis (EDX) was carried out to look for small amounts of phase which did not appear in the x-ray powder diffraction patterns. The results showed that the high- T_c compositions contained less than 5% of unreacted CuO. Sintering at high temperature, $T > 890^\circ\text{C}$, deteriorated the superconducting properties. In this temperature range, the pellets melted and the $\text{Bi}_2(\text{SrCa})_2\text{Cu}$ (2201) phase was formed.

In this experiments, The high- T_c phase was only produced in high purity from the CuO-rich composition, $\text{BiSrCaCu}_3\text{O}_x$. Long reaction time and precise temperature control within a few degree of the solidus temperature seemed to be essential to form high- T_c phase. The superconducting properties deteriorated on partial melting or softening of pellets.

Critical temperature measurement

Critical temperature measurements were carried out to monitor high- T_c phase formation. For the nominal starting compositions, which were sintered at $880 \pm 5^\circ\text{C}$ for several days, the temperature dependence of resistivity was measured. The results are shown in table 4.

A single transition with onset at around 105K was observed in the CuO-rich nominal composition 2 : 2 : 2 : 4 (Bi : Sr : Ca : Cu). The

Table 4. Starting Compositions and Characteristics.

No	Starting composition ratio (Bi : Sr : Ca : Cu)	Time (days)	T_c^* (zero resistance of tail)
1	2 : 2 : 2 : 4	30	105K
2	2 : 2 : 2 : 3	30	30.80K
3	3.5 : 4 : 4 : 3	14	92(76K)
4	4 : 4 : 3 : 3	14	89(76K)
5	2 : 1.8 : 2 : 3	14	83(60K)

*Midpoint of transition

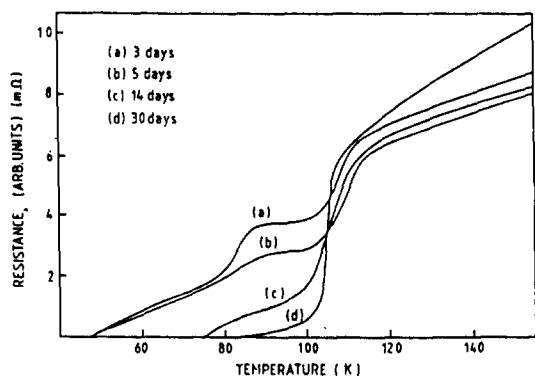


Fig. 7. Temperature dependence of electrical resistance for $\text{BiSrCaCu}_2\text{O}_x$ samples sintered at $880 \pm 5^\circ\text{C}$ in air as a function of various reaction times. The specimen (d) shows midpoint T_c 105K with narrow tail from 80 K.

ideal composition of 2 : 2 : 2 : 3 showed two transition steps at 30 and 80K. The other starting compositions showed a transition with onsets at around 90K with long resistance tails to low temperature, but with no evidence of the 105K transition.

In order to investigate the effect of reaction time upon the formation of the high- T_c phase ($T_c > 100\text{K}$), a fresh specimen of $\text{BiSrCaCu}_2\text{O}_x$ composition was reacted for 30 days at $880 \pm 5^\circ\text{C}$. Resistance measurements were carried out every 1–2 days to monitor the formation of the high- T_c superconducting phase, figure 7. The fraction of high- T_c phase increased with reaction time. After 30 days reaction, a sharp superconducting transition with midpoint at around 105K was observed but there was still some small but measurable residual resistance down to 80K.

The stability of the 110K phase was investigated by annealing at high temperatures. No significant change in resistive behaviour was observed on annealing in the approximate temperature range $700\text{--}800^\circ\text{C}$. The pellet was then crushed, reground, pressed into a fresh pellet

and refired in order to reduce its porosity. After firing at $800\text{--}850^\circ\text{C}$ in air for 48 hours the sharp transition at $\approx 100\text{K}$ disappeared and was replaced by a broad transition from 80 to 100K. X-ray powder diffraction confirmed the loss of the high- T_c phase. This result indicated the high- T_c phase is kinetically stable up to 800°C , but thermodynamically stable very close to the formation temperature.

Oxygen content measurement

Oxygen stoichiometry is important in determining the critical temperature, T_c . The critical temperature of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212 phase) was very sensitive to oxygen content and could be varied by annealing the sample at different temperature and oxygen partial pressures.

Tallon et al.^{6,23)} reported that the high- T_c (2223) phase requires oxygen stoichiometry has been observed while oxygen loading to maximize critical temperature. A large variation in T_c depending on oxygen stoichiometry has been observed while oxygen stoichiometry hardly affects the critical temperature in the Pb substituted 2223 phase²⁵⁾. The oxygen content of the Pb-free 2223 phase has not been measured because of difficulties in preparing phase pure samples. The excess oxygen content of an almost single phase samples of composition $\text{BiSrCaCu}_2\text{O}_{11+x}$ (1 : 1 : 1 : 2) has been determined by citrate iodometry, table 5.

This corresponds to an apparent average copper valence of 2.22 which is similar to that in $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8.19}$ (2212), 2.19, but lower than that in $\text{Bi}_{2.3}\text{Sr}_{1.7}\text{CuO}_{6.13 \pm 0.18}$ (2201), 2.36²⁹⁾

Discussion

It has been reported by several workers that doping the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ composition with Pb promotes the formation of the high- T_c phase^{2,28,30)}. There is some doubt about the role of Pb is its

Table 5. Excess Oxygen Content Measured by Iodometry Method

Nominal composition	Formal Copper valence value	Excess oxygen content(x)
$\text{BiSrCaCu}_2\text{O}_{11+x}$	2.22 ± 0.03	0.33 ± 0.04

incorporation in the Bi-O layers, or simply it being a flux during the high temperature sintering process. Most, but not all, of the Pb evaporates during the heat treatment^{30, 31)}. It is interesting to note that the introduction of Pb as a substitutional impurity shortens the C axis by about 0.4 Å compared to that of Pb-free high- T_c phase. Partial Pb substitution into the weak interlayer Bi-O bonding is believed to be responsible for enhancing crystal growth along the C axis. This modification stabilises the high- T_c phase and facilitates its formation at lower temperature.

From x-ray powder diffraction data, together with electrical resistivity measurements, Pekker et al³²⁾ proposed that 2201 and 2212 are equilibrium phases at room temperature. The 2223 phase would be stable above around 880 °C, and only metastable at room temperature. High temperature x-ray diffraction indicated that the 2212 phase disappears above 870°C whereas the 2223 phase seems to remain stable up to 890°C³³⁾. Narumi et al²²⁾ also suggested that the Pb doped high- T_c phase seems to be in a metastable state from observation of the reduction of T_c after a few days.

The critical temperature of the Pb-doped high- T_c phase has been measured by several authors^{16, 18~21)}. Results showed that the addition of Pb eliminates the long tail resistance, even though midpoint critical temperatures change little. Recently Wu et al³⁴⁾ investigated the structural and electronic effects of Pb-substitution by scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS). Large area STM images of the Bi(Pb)-O layers showed that lead substitution distorts and disorders the one-dimensional superlattice; however, STS data showed that the electronic structure was insensitive to lead substitution. The superconducting transition temperatures were independent of x ($x < 0.7$) in $Pb_xBi_{2-x}Sr_2CaCu_2O_{8-\delta}$. This suggested that the lead-induced electronic and structural changes in the Bi(Pb)-O layer do not perturb the elec-

tronic states critical to forming the superconducting state in this system. The substituted lead seems to accelerate the kinetics of phase formation and extend the domain of high- T_c phase. The narrow long tail from Pb-free phase is thought to be due to the existence of weak links between the grains of high- T_c phases in the ceramic^{28, 30)}.

The details of the phase formation of the high- T_c crystals are not clear, but the long reaction time just below melting point required for phase formation seems to be important in considering the formation mechanism. The difficulty in forming the high- T_c phase may arise simply from the similarity of the structures in the bismuth phases and hence a lack of thermodynamic driving force.

4. Conclusions

Phase formation in the Bi-Sr-Ca-Cu-O system has been investigated. Samples were prepared by solid state reaction of the oxides, using reaction times of several days and temperatures in the range 600–900°C.

1) The 80K superconducting phase (2212) was successfully prepared with nominal composition 2:2:1:2 (Bi:Sr:Ca:Cu) using solid state synthesis. The x-ray powder diffraction pattern was fully indexed. There was no unexplained weight loss (<0.1%) during either the reaction or subsequent annealing treatments.

2) An area of 2212 based solid solution formation given by the formula $Bi_2Sr_{2-x}Ca_{1+y}Cu_2O_{8-\delta}$, where $0 < x < 0.3$ and $0 < y < 0.3$, was obtained as a single phase. The dependences of oxygen content and lattice parameter upon composition clearly showed the existence of a solid solution.

3) The high- T_c superconducting phase was obtained almost phase pure from the nominal composition of $BiSrCaCu_2O_x$. The conditions for the preparation of the high- T_c phase were very critical, because of the long range diffusion needed and especially its narrow temperature stability domain. The high- T_c phase was

produced only after a long time of reaction(30 days) at a temperature, $880 \pm 5^\circ\text{C}$, close to but just below melting. From the results of this work, the 015K superconduction phase was only produced from Cu-rich compositions ; however, a superconducting transition at 105K always contains a long resistance tail, perhaps associated with the presence of small amounts of impurities at the grain boundaries.

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