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Physica C 276 (1997) 75–83

PHYSICA C

Structural and superconducting properties of phases in the underdoped $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$ system: The evidence for a chemical pressure effect

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Received 18 November 1996

Abstract

An attempt was made to investigate the chemical pressure effect (i.e., smaller isovalent cation substitution) on the superconductivity of phases in the $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$ (Sr-doped 247) system. A series of Sr-doped 247 phases with $x = 0, 0.05, 0.10, 0.15, 0.175, 0.20$ and 0.30 were prepared under 20 bar of oxygen at 900°C , followed by thermal annealing under 100 bar of oxygen at 300°C and slowly cooled down to ambient temperature. The solubility limit of Sr in the 247 phase was found to be ca. 0.10 to 0.15 and the orthorhombic lattice distortion for the Sr-doped 247 phases increased with increasing Sr content, as determined from X-ray diffraction (XRD). Rietveld refinement based on the XRD data obtained for $Y_2(Ba_{0.9}Sr_{0.1})_4Cu_7O_{14.74}$ indicated that 92.5% of Sr atoms substituted for the Ba sites in the $YBa_2Cu_4O_8$ subcell. The T_c of the Sr-doped 247 phases increased from 72 K ($x = 0$) to 75 K ($x = 0.10$) monotonically upon Sr substitution, as indicated by both dc resistivity and magnetic susceptibility data. The dopant composition coefficient of T_c , dT_c/dx , for the series of Sr-doped 247 phases with $0 \leq x \leq 0.10$ was also determined to be +7.5 K per Sr atom per formula unit based on magnetic susceptibility data. We have demonstrated that the principle of chemical pressure effect can be applied to enhance T_c in a series of Sr-doped 247 phases without applying high physical pressure.

Keywords: High-pressure synthesis; Underdoped $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$; Rietveld refinement; Electrical resistivity; Chemical pressure effect

1. Introduction

The $Y_2Ba_4Cu_7O_{14+\delta}$ (247 phase) with a superconducting transition temperature (T_c) at ca. 40 K was first observed by Karpinski et al. [1] as an impurity phase in the investigation of a pressure-temperature-composition phase diagram in the system of $YBa_2Cu_3O_{6+x}-O_2$. Bordet et al. [2] were

then able to grow single crystals of the 247 phase and determined its crystal structure. Being an ordered intergrowth structure of alternating units of $YBa_2Cu_3O_{6+x}(123)$ - and $YBa_2Cu_4O_8(124)$ -type building blocks, and consisting of intervening single and double chains formed by CuO_4 square-planar units along the b -axis, the 247 phase possesses a unique yet relatively complicated structure among the homologous $Y_2Ba_4Cu_{6+n}O_{14+n}$ ($n = 0, 1, 2$) series. Another interesting aspect of the 247 phase is that its T_c falls rapidly with decreasing oxygen con-

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tent from the single CuO_2 chains in the 123 subunit with that of the 124 subunit remaining intact, and the T_c -dependence of the oxygen composition has been investigated by Genoud et al. [3]. There have been numerous reports regarding investigations of the correlation between superconductivity (i.e., T_c) and the hole concentration in the Cu-O planes and/or the relative oxygen stoichiometry in the CuO_2 chains in the yttrium-based 123 and 124 phases by atomic substitution. Particularly, the substitution of Ca for Y or Ba and La for Ba, respectively, has been investigated by a number of research groups [4–10]. For instance, the enhancement of T_c from 83 to 90 K by 10% Ca substitution for Y in the 124 phase was first reported by Miyatake et al. [9] and later was confirmed by several research groups [10,11]. The attempts to substitute Ca for Y and Ba sites, and La for Ba sites in 247 phase (i.e., $\text{Y}_{2-1.5x}\text{Ba}_{4-0.5x}\text{Ca}_{2x}\text{Cu}_7\text{O}_{15-y}$, $\text{Y}_2(\text{Ba}_{1-x}\text{La}_x)_4\text{Cu}_7\text{O}_{15-y}$) were reported by Buckley et al. [12]. Recently, Triscone et al. [13] reported the substitution of Ca on the Y and Ba sites to form $(\text{Y}_{1-x}\text{Ca}_x)_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ and $\text{Y}_2(\text{Ba}_{1-x}\text{Ca}_x)_4\text{Cu}_7\text{O}_{14+\delta}$ phases, respectively, and found that samples were not monophasic for $x > 0.05$, and that Ca entered preferentially into the Ba sites. Interestingly, the authors did not observe an increase of T_c as a result of Ca substitution. However, isovalent cation substitution in the yttrium-based high- T_c phases has been investigated less frequently. T_c values of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ phases with $0 \leq x \leq 0.60$ were nearly constant, being around 80 K, whereas T_c values of $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_7$ decreased with increasing Sr content, as reported by Wada et al. [14]. The latter observation was consistent with those obtained in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_7$ system reported by Sung et al. [15]. Karen et al. [16] observed a chemical pressure effect in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{6.948}$ ($0 \leq x \leq 0.35$) series whose dT_c/dP and dT_c/dx were found to be 0.7 K/GPa and $-20(2)$ K/Sr atom, respectively. On the contrary, Liu et al. [17] observed a T_c increase from 85 K to 90 K in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ system with $x = 0.1-0.2$ and then decreased to 64 K at $x = 0.5$, which was attributed to a chemical pressure effect, i.e., change of T_c due to substitution of a small isovalent cation for a larger ion site. Nonetheless, to our knowledge the isovalent cation substitution in the 247 phase attempted to study the chemical pres-

sure effect has not been reported so far. Structurally, there exist one Y, two Ba and four Cu sites of crystallographic distinction available for cation substitution. This structural feature added a certain degree of complexity to the investigation on the atomic substitution, particularly for Ba or Cu sites in the 247 phase, and thus it merits close attention.

This research was motivated by the reported attempts to investigate the effect of chemical pressure on superconductivity. Based on our investigations the principle of chemical pressure can effectively provide another alternative to significantly enhance T_c of underdoped HTSC's without employing an extra-high pressure technique. In this paper we report the preparation of a series of monophasic Sr-doped 247 samples with $0 \leq x < 0.15$ by a high-pressure technique, and the investigation of a systematic trend in Sr solubility in the 247 phase, variation of crystallographic parameters and T_c upon isovalent Sr-substitution for Ba and relevant rationalizations were also proposed.

2. Experimental

A series of Sr-doped 247 samples with nominal composition $\text{Y}_2(\text{Ba}_{1-x}\text{Sr}_x)_4\text{Cu}_7\text{O}_{14+\delta}$ and with $x = 0, 0.05, 0.10, 0.15, 0.175, 0.20$ and 0.30 were prepared by reacting stoichiometric amount, of high purity Y_2O_3 , BaO, SrO and CuO (Cerac, U.S.A.) using a commercial high-pressure oxygen furnace [18]. The reaction mixtures were preheated at 866–910°C for four days with three intermittent grindings in the air. Further sintering was then carried out twice at 990–995°C for two days under 20 bar of oxygen atmosphere. The samples were then naturally cooled in the furnace to 300°C by switching off the power to avoid the formation of the 124 phase. Finally, the samples were then annealed at this temperature for 2–3 days under 100 bar of oxygen so that the samples were fully loaded with oxygen.

The determination of the phase purity was carried out by powder XRD on a MAC Science MXP-3 automatic diffractometer equipped with a Ni-filter and Cu $K\alpha$ radiation. The lattice constants of the Sr-doped 247 phases were determined based on XRD patterns by using a least-squares refinement program LATT [19]. Rietveld refinement on the powder X-ray

diffraction pattern of a $Y_2(Ba_{0.9}Sr_{0.1})_4Cu_7O_{14.74}$ sample was carried out by using the computer program DBWS-9600PC provided by Wiles and Young [20]. The electrical resistivity of the Sr-doped 247 samples as a function of temperature was measured by a conventional dc four-probe method using a 10 mA current on an RMC model 22C closed-cycle cryogenics system equipped with a Si-diode temperature sensor. The temperature-dependence of field-cooled (20G) dc magnetic susceptibility using an automatic SQUID magnetometer (MPMS system, Quantum Design, U.S.A.).

3. Results and discussion

The comparison of XRD patterns of Sr-doped samples with nominal composition $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$ and with x : (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.175, (f) 0.20 and (g) 0.30, respectively, is represented in Fig. 1. All of the Sr-doped 247 samples with $x = 0, 0.05$ and 0.10 were determined to be monophasic according to powder XRD analysis. However, in addition to trace impurity phases such as CuO and SrO, $YBa_2Cu_4O_8$ (124 phase) was

found to be the major phase in the samples with $x \geq 0.15$ (i.e., Figs. 1d–g), the solubility limit of Sr in the 247 phase was very likely to lie in the range of $0.10 < x < 0.15$. In the Sr-overdoped phase with $x = 0.15$, the 124 and 247 phases were found to coexist in the sample. These results were found to be much lower than the values of 0.30 and 0.60 reported for the $Y(Ba_{1-x}Sr_x)_2Cu_4O_8$ (prepared by chemical coprecipitation) [17] and $Y(Ba_{1-x}Sr_x)_2Cu_3O_z$ (synthesized by solid-state reactions) [14] systems, respectively. The difference in the solubility limit of Sr in the three yttrium-based 123, 124 and 247 phases described above can presumably be very sensitive to the methods by which samples were prepared and, therefore, the solubility of Sr appears not to be an intrinsic crystal chemical property of the 247 phase. Furthermore, shown in the inset of Fig. 1 we have highlighted a systematic shifting of major reflections (e.g., (1 0 12), (0 0 18), (0 1 13), (111), (113) and (115)) toward larger 2θ , which strongly indicates that Sr atoms entered the two crystallographically independent Ba sites in the 247 lattice presumably in a distorted fashion.

In order to study the effect of Sr substitution on the crystallographic properties of the Sr-doped 247

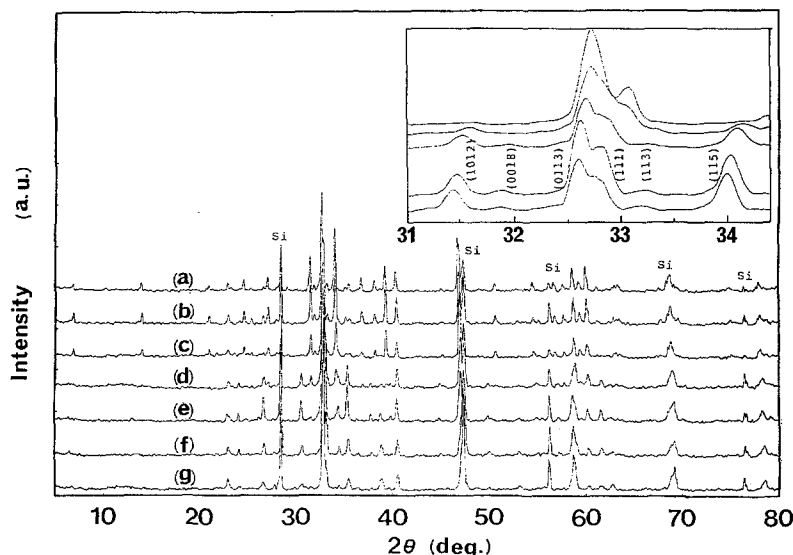


Fig. 1. Comparison of XRD patterns of $Y_2(Ba_{1-x}Sr_x)_4Cu_7O_{14+\delta}$ samples with x : (a) 0, (b) 0.05, (c) 0.10, (d) 0.15, (e) 0.175, (f) 0.20 and (g) 0.30 with Si added as an internal standard. Trace impurities such as CuO and SrO started to appear in samples (d) through (g). The inset indicates a systematic shifting of six major diffraction peaks toward higher 2θ .

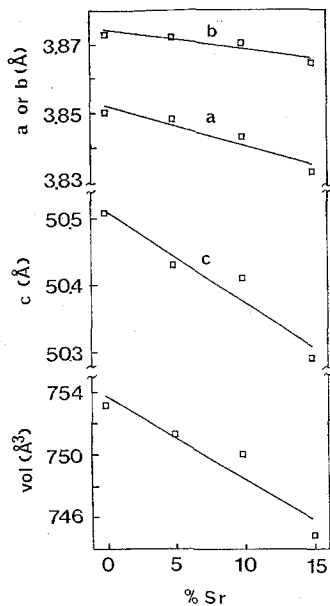


Fig. 2. Lattice parameters a , b , c and cell volume of Sr-doped 247 phases determined from XRD patterns with respect to Sr content (x).

phases, the lattice parameters a , b , c and cell volume of Sr-doped 247 phases determined from XRD patterns with respect to Sr content (x) are represented in Fig. 2. Our lattice parameter data for the parent 247 phase ($x = 0$) were in better agreement with those reported by Morris et al. [21] than those determined by Bordet et al. [2] and Karpinski et al. [22], respectively. The lengths of c - and a -axes were found to shorten significantly from 50.509(9) to 50.29(1) Å and 3.850(1) to 3.833(1) Å, respectively, but the b -axis remains more or less unchanged as the Sr content increases from 0 to 0.15. Furthermore, the unit cell volume was found to decrease from 753.1(3) Å³ ($x = 0$) to 744.9(1) Å³ ($x = 0.15$) as more and more smaller Sr cations gradually entered the Ba sites. The extent of lattice shrinkage was estimated to be 0.28, 0.14 and 3.39 ppt per Sr-atom per formula unit for the crystallographic a -, b - and c -axes, respectively, for $0 \leq x \leq 0.15$. These observations can be rationalized by considering the difference in ionic radii of Ba²⁺ (1.52 Å) and Sr²⁺ (1.36 Å) [23] and the relatively rigid double-chain structure (along the b -axis direction) of the 247 lattice. The latter factor presumably causes the b -axis to be less sensitive to

the size reduction of the substituent cations and, therefore, b shrunk less than the a - or c -axis. In addition, the different extents of shrinkage in the lattice dimensions of the Sr-doped 247 phases also indicated that, unlike the physical pressure, the effect of chemical pressure on lattice dimensions is rather anisotropic.

On the other hand, Fig. 3 shows that the orthorhombic distortion, represented by $(b - a)/(b + a)$, in the lattice of the Sr-doped 247 series increases with increasing Sr substitution which is similar to the trend observed in both the Y(Ba_{1-x}Sr_x)₂Cu₄O₈ ($0 \leq x \leq 0.30$) [17] and the Ca- and La- substituted 247 systems [12], yet contradicting the behaviour reported on the Y(Ba_{1-x}Sr_x)₂Cu₃O_z ($0 \leq x \leq 0.60$) system [14]. The trend of increasing orthorhombicity with increasing Sr content in the Sr-doped 247 samples could presumably be attributed to the disordering of oxygen atoms driven by Sr substitution between the oxygen sites distributed within or between the CuO chains of the 123 sublattice, for unknown reasons.

The structure refinement using the Rietveld technique was carried out on the Y₂(Ba_{0.9}Sr_{0.1})₄Cu₇O_{14.74} sample and was initiated from the model of orthorhombic Y₂(Ba_{1-x}Sr_x)₄Cu₇O_{14+δ}. The occupancy of the Ba sites was fixed at 3.60. Good agreement between the observed and calculated patterns was obtained as shown in Fig. 4. The final results of the Rietveld refinement on the Y₂(Ba_{0.9}Sr_{0.1})₄Cu₇O_{14.74} compound are presented in Table 1. Interestingly, 92.5% of the Sr atoms were found to enter the Ba(2) site (of the 124 substructure) and the rest of the Sr atoms were found to substitute for the Ba(1) site (of the 123 substructure),

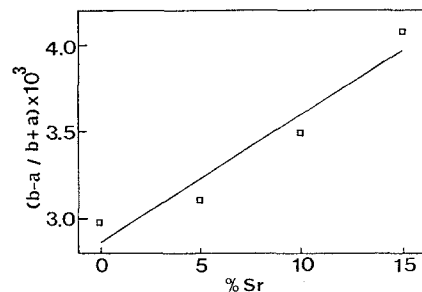


Fig. 3. The orthorhombic distortion of Sr-doped 247 phases as a function of Sr content (x).

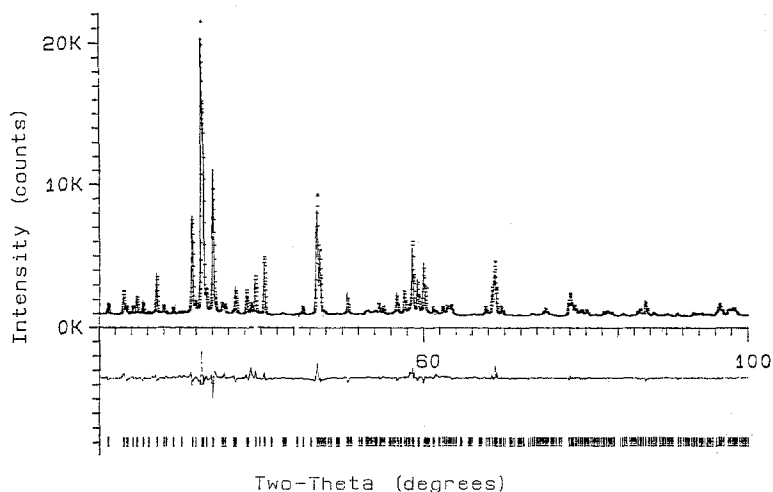


Fig. 4. Rietveld refinement on the XRD pattern for $Y_2(Ba_{0.9}Sr_{0.1})_4Cu_7O_{14.74}$ at room temperature. The — symbols represent raw data points (top) and a continuous line (top) shows the calculated patterns. The pattern in the middle is the difference between the observed and calculated intensities. The bars shown in the bottom represent the calculated pattern.

as indicated by powder Rietveld refinement. This observation may be attributable to the difference in the size and coordination environment of the Ba(1) and Ba(2) sites and it could probably be rationalized with the results of the crystal lattice energy calculations including both Sr and Ba atoms.

The temperature dependence of the resistivity for the monophasic Sr-doped 247 samples with $x = 0, 0.05, 0.10$ and 0.15 (containing impurities of the 124 phase) is presented in Fig. 5. In the homogeneity region of Sr-substitution, all the samples exhibited metallic behavior in their normal state with resistiv-

Table 1

The final results of Rietveld refinement by using X-ray diffraction data for $Y_2(Ba_{0.9}Sr_{0.1})_4Cu_7O_{14.74}$ at room temperature. The B (nm^2), N , R and R_w are isotropic thermal parameters, occupancy, averaged and weighted disagreement factors, respectively. (Space group: Ammm; $R = 4.15\%$, $R_w = 5.94\%$.) Numbers in parentheses are estimated standard deviation of the last significant digits

Atom	x	y	z	B	N
Y	0.5	0.5	0.1151(1)	0.46(8)	2
Ba(1)	0.5	0.5	0.0426(1)	1.99(11)	1.97(3)
Sr(1)	0.5	0.5	0.0426(1)	1.99(11)	0.03(3)
Ba(2)	0.5	0.5	0.1881(1)	1.26(9)	1.63(3)
Sr(2)	0.5	0.5	0.1881(1)	1.26(9)	0.37(3)
Cu(1)	0	0	0	1.9(3)	1
Cu(2)	0	0	0.0821(1)	0.39(13)	2
Cu(3)	0	0	0.1478(1)	0.89(15)	2
Cu(4)	0	0	0.2307(1)	1.24(15)	2
O(1)	0	0	0.0398(4)	1.0	2
O(2)	0.5	0	0.0842(4)	1.0	2
O(3)	0	0.5	0.0887(3)	1.0	2
O(4)	0.5	0	0.1463(4)	1.0	2
O(5)	0	0.5	0.1461(3)	1.0	2
O(6)	0	0	0.1952(3)	1.0	2
O(7)	0	0.5	0.2348(4)	1.0	2
O(8)	0	0.5	0	1.0	0.21(2)
O(9)	0.5	0	0	1.0	0.53(2)

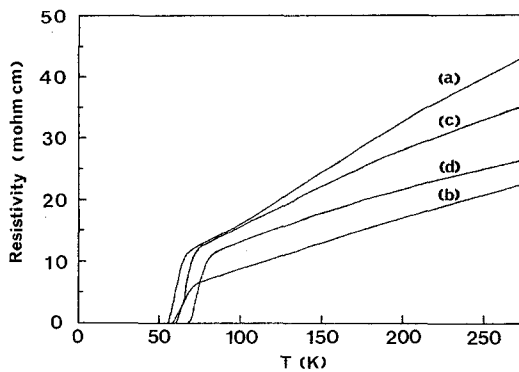


Fig. 5. Temperature dependence of electrical resistivity of Sr-doped 247 phases with respect to Sr content x .

ity at 298 K, $\rho(298\text{ K})$, equal to 2.4–4.5 m Ω cm. We have also noted that the magnitude of $\rho(298\text{ K})$ decreases with increasing Sr content except for the sample with $x = 0.05$ that exhibited the lowest $\rho(298\text{ K})$ amongst all samples. The resistive $T_{c(\text{onset})}$ of the parent 247 phase ($x = 0$) with oxygen content of 14.78, as determined by a thermogravimetric analysis, was found to be 70 K which is in good agreement with that reported by Genoud et al. [3].

As the amount of doped Sr increased, T_c of the Sr-doped 247 phases was found to increase significantly from $T_{c(\text{onset})} = 70\text{ K}$ ($x = 0$) to $T_{c(\text{onset})} = 75\text{ K}$ ($x = 0.10$) with a broad resistive transition of 12–14 K for the individual sample. This observation can

probably be attributed to sample inhomogeneity, typically inherited from synthetic techniques employing high-temperature and high-pressure conditions. Similar observations have also been reported in the Sr-doped $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ samples [17].

To ensure bulk superconductivity of the Sr-doped 247 samples we have investigated the temperature dependence of low-field (20 G) dc magnetization (Meissner effect) for a series of powder samples having the compositions $\text{Y}_2(\text{Ba}_{1-x}\text{Sr}_x)_4\text{Cu}_7\text{O}_{14+\delta}$ ($0 \leq x \leq 0.15$) and the results were presented in Fig. 6. The diamagnetic signals for the Sr-doped 247 samples with $x = 0, 0.05$ and 0.10 , appeared at 72, 73.6 and 75 K, respectively. The T_c of 84 K observed in the sample with $x = 0.15$ (Fig. 5) was attributed to the presence of the $\text{YBa}_2\text{Cu}_3\text{O}_8$ phase. These values are approximately consistent with the onset of superconductivity obtained from dc four-probe electrical resistivity measurements.

Furthermore, in this homogeneity range the superconducting volume fraction of the Sr-doped 247 samples increases with increasing Sr dopant content. This observation is in good agreement with those observed by Liu et al. [17], but in contrast to those reported by Wada et al. [14]. The trend observed in the T_c dependence of the Sr dopant concentration in this work can probably be attributed to the stronger coupling between the Cu-O layers in either or both the 123 and 124 subunits, resulting directly from the

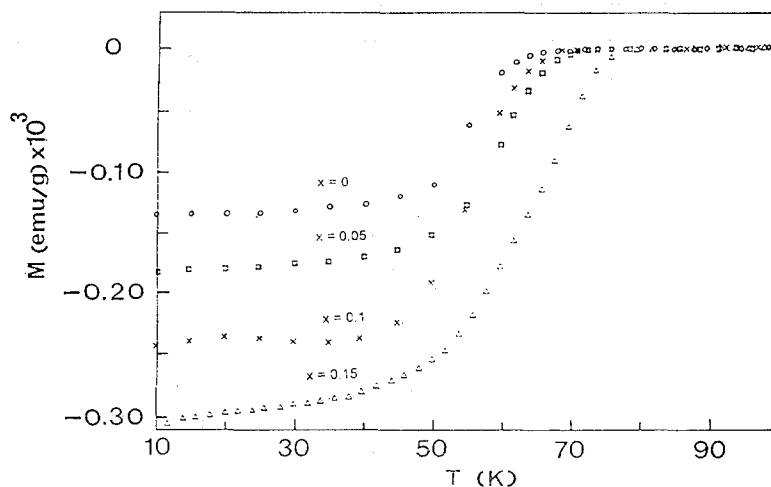


Fig. 6. Temperature dependence of field-cooled (20 G) dc magnetic susceptibility of samples with $x = 0, 0.05, 0.10$ and 0.15 .

shortening of the c -axis that was driven by isovalent Sr substitution. On the other hand, substituting the smaller Sr for Ba in the 247 phase may have an equivalent effect on T_c , similar to applying high pressure on the crystal lattice, which could lead to an enhanced charge transfer from the single or double Cu-O chains to the CuO_2 planes and caused T_c to increase up to its optimal values according to Tallon et al. [24] and Yamada et al. [25].

The T_c values for the Sr-doped 247 phases determined from the diamagnetic transition temperature and those reported for the Sr-doped 123 and 124 phases as a function of Sr content are plotted in Fig. 7 for comparison. We found that T_c for the Sr-doped 247 phases varies from 72 to 75 K monotonically across the entire solubility range ($x \leq 0.10$) with increasing Sr content. The rate at which T_c increases as a function of dopant stoichiometry (i.e., dT_c/dx) was found to be $+7.5$ K/Sr atom per formula unit which is much smaller than the absolute value of the rate at which T_c decreased (e.g., $dT_c/dx = -45$ K/Sr atom) observed in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ phases with $0.3 \leq x \leq 0.5$; but larger than that (e.g., $dT_c/dx = -10$ K/Sr atom) estimated in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_z$ system ($0 \leq x \leq 0.60$) [14].

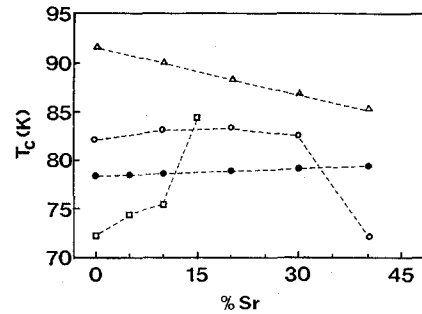


Fig. 7. The trend of $T_{c(\text{mid})}$ variation for the Sr-doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Δ) [14], $\text{YBa}_2\text{Cu}_4\text{O}_8$ (\bullet) [14] and \circ [17], respectively) and $\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$ (\square) phases as a function of Sr substitution. Dashed lines connecting data points are simply a guide for the eye.

Furthermore, the pressure coefficient or pressure dependence of T_c (dT_c/dP) can generally be considered as an index revealing how sensitively the T_c values of these yttrium-based phases respond to the change of pressure or equivalent effect similar to pressure changes (e.g., smaller cation substitution in the crystal lattice). In order to compare and understand the effect of physical and chemical pressure on T_c for a variety of parent and Sr-doped 123, 124 and

Table 2

Comparison of dT_c/dP and dT_c/dx for a variety of parent and Sr-doped 123, 124 and 247 phases indicating the effect of physical and chemical pressure on T_c of three yttrium-based cuprate superconductors

Compounds	dT_c/dP (K/GPa)	dT_c/dx (K/Sr atom)	Reference
$\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$			
$\delta = 0$	0.4	–	[26]
$0.2 \leq \delta \leq 0.6$	4.3 ± 0.7	–	[26]
$\delta = 0.65$	8	–	[26]
$\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_{7-\delta}$			
$0 \leq x \leq 0.6$	–	–9.2	[14]
$\text{YBa}_2\text{Cu}_4\text{O}_8$	$5.5 (P < 15 \text{ KPa})$		[28]
$\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$			
$0 \leq x \leq 0.2$	–	12.6	[17]
$0.2 \leq x \leq 0.5$	–	–43.3	[17]
$0 \leq x \leq 0.4$	–	3.75	[14]
$\text{Y}_2\text{Ba}_4\text{Cu}_7\text{O}_{14+\delta}$			
$\delta = 0$	3.0	–	[27]
$0.4 \leq \delta \leq 0.9$	4.9	–	[27]
$\text{Y}_2(\text{Ba}_{1-x}\text{Sr}_x)_4\text{Cu}_7\text{O}_{14+\delta}$			
$0 \leq x \leq 0.15, \delta = 0.78$	–	7.5	this work

247 phases, we have tabulated the values of dT_c/dP and dT_c/dx reported or derived from our work for the three yttrium-based phases in Table 2 for comparison. For instance, the reported pressure dependence of T_c (i.e., dT_c/dP) for the 123, 247 and 124 phases varies from 0.4 [26], 3.0 (or 4.9 [27]), to 5.5 K/GPa [28], respectively, which reveals a close correlation with dT_c/dx of the Sr-doped 123, 247 and 124 systems, whose values were estimated to be -9.2 [14], 20 and $12.6-43.3$ [17] K/Sr atom, respectively.

We have also established that the effect of substituting one Sr-atom per formula unit is equivalent to applying an external pressure of 1.53 GPa (for $0 \leq x \leq 0.10$) on the T_c of the Sr-doped 247 phases by assuming that both of the parent and Sr-doped 247 phases have the same value of dT_c/dP . The dT_c/dP data described above have been proposed to be due to a difference between the hole concentration of the Cu-O planes and chains and difference in the lattice orthorhombicity by Tallon et al. [24] and Scholtz et al. [29]. Our investigation has also clearly indicated the close and parallel correlation between dT_c/dP and isovalent-dopant concentration coefficient of T_c (e.g., dT_c/dx). On the other hand, since the stronger coupling between the CuO_2 planes perpendicular to the c -axis in the Sr-doped 247 phase is expected due to Sr substitution, it will be interesting to investigate the dopant concentration dependence of critical current density (J_c) for the Sr-doped 247 samples which is currently in progress in our laboratory.

4. Conclusion

We have successfully prepared a series of monophasic $\text{Y}_2(\text{Ba}_{1-x}\text{Sr}_x)_4\text{Cu}_7\text{O}_{14+\delta}$ samples with $0 \leq x \leq 0.10$ by solid-state reactions under high-pressure of oxygen, and the solubility limit of Sr in the 247 phase was also determined to be between 0.10 and 0.15 per formula unit. We found that the dimension of the unit cell decreased upon Sr substitution, yet orthorhombic distortion of the unit cell was found to increase monotonically with increasing Sr-dopant content. Both dc resistivity and dc magnetic susceptibility measurements showed that the T_c of the Sr-doped 247 phases rose from 72 ($x = 0$) to 75 K ($x = 0.10$) with dT_c/dx estimated to be $+7.5$

K/Sr atom per formula unit. We have observed that there exists a chemical pressure effect on the superconductivity in the Sr-doped 247 series.

Similar results have also been observed by Liu et al. [17] and Wada et al. [14] in the $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ ($0 \leq x \leq 0.30$) series, respectively. However, results obtained from investigations in both $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_3\text{O}_7$ ($0 \leq x \leq 0.60$) and $\text{Y}(\text{Ba}_{1-x}\text{Sr}_x)_2\text{Cu}_4\text{O}_8$ ($0.3 \leq x \leq 0.50$) systems contradicted our observations. We have also noticed a correlation between dT_c/dx and dT_c/dP in the parent and three Sr-doped yttrium-based phases and the rationalizations require further studies. The principle of the chemical pressure effect can be applied to offer a new alternative to enhance T_c of oxide superconductors without employing the extra-high pressure technique.

Acknowledgements

We thank the National Science Council of Taiwan for financial support through grants No. NSC85-2113-M-009-010 and NSC83-0115-C009-01-008M and the Regional Instruments Center of NSC in Hsinchu for the magnetization measurements. D.H. Chen is acknowledged for carrying out the X-ray Rietveld refinement. A summer undergraduate traineeship given to TRL by NSC is also acknowledged.

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