

Substitution Effects of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+z}$ ($\text{M}=\text{Co}, \text{Ni}$) Single Crystals[†]

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Single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+z}$ superconductors doped with Co and Ni have been prepared by the travelling-solvent-floating-zone (TSFZ) method. The measured concentration of M/Cu is 2.3%, 4.0%, 5.5% for M=Co and 2%, 5% for M=Ni. It is found that the c-axis shrinks with the increasing concentration of the doping element. The critical temperature T_c is sharply depressed by the substitution of both elements with an initial rate of about 5 K per percentage doping. The influence of the doping elements as impurities on the different pinning regimes of Bi-2212 single crystals is discussed.

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Substitution of Cu by 3d-elements in the high- T_c cuprate oxides affects directly the superconducting layers and is therefore an effective way for studying the superconductivity mechanism. Most of the studies on Bi-2212 system are on polycrystalline samples [1-4], which show that 3d-elements depress the transition temperature T_c sharply. The decrease of T_c has been attributed to impurity-induced pair breaking [2,4], or to the influence of excess oxygen-content caused by the substitution [3,5]. Because of the sensitivity of T_c for the impurity concentration, it is of importance to grow single crystals uniformly doped with 3d-elements. Single crystals of Bi-2212 doped with Co, Fe, Ni and Zn grown by the self-flux method have been studied in [5-6]. Crystal growth by the TSFZ method has also been reported for Bi-2212 with partial substitution up to 3% Fe (7) and up to 2% Ni [8].

Another issue of great interest is the pinning mechanism of the high- T_c superconductors. In the high- T_c superconductors several types of defects, such as oxygen deficiencies and twin boundaries, have been demonstrated to attribute to the pinning strength. Since substitution of Cu by 3d-elements introduces point defects in the Cu-O planes, its influence on the critical current density j_c could give some insight in the pinning mechanism of Bi-2212. In a recent study for Fe, Ni and Zn doped Bi-2212 single crystals a decrease of j_c has been reported [6].

In this work we have used the TSFZ technique to grow single crystals of Bi-2212 with substitution of Co and Ni for Cu. The nominal concentration of Co is 1%, 2% and 5%; of Ni

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is 2% and 4%. Generally more homogeneous single crystals, with higher j_c , can be obtained by TSFZ method as compared to the crucible method. The effects of the substitution on the structure, T_c , as well as j_c were investigated.

The single crystals of $\text{Bi}_2\text{Sr}_2\text{Ca}(\text{Cu}_{1-x}\text{M}_x)_2\text{O}_{8+x}$ with $M=\text{Co}$ and Ni were grown by TSFZ method. Powders of Bi_2O_3 , CaCO_3 , SrCO_3 , CuO and $\text{Co}(\text{C}_2\text{O}_4)\cdot x\text{H}_2\text{O}$, or NiO were mixed in the appropriate ratio and sintered twice at 860 °C in flowing oxygen for 24 hours with intermediate grinding. Bars with 8 mm diameter made from the obtained powders were isostatically pressed at 3 kbar and then sintered at 865 °C in flowing air for 24 hours. The sintered bars were zone melted in a home built optical radiation furnace [9]. A pulling rate of 80 mm/h was first used for improving the density of the bars. Then the densified bars were zone melted with a low pulling rate of 1 mm/h under an atmosphere of 2 bar flowing air. Doping with the 3d-elements reduces the size of the single crystals to a typical dimension of $3 \times 1.5 \times 0.15 \text{ mm}^3$ from a typical size of $10 \times 3 \times 0.3 \text{ mm}^3$ for the pure Bi-2212 single crystals (The c-axis is along the smallest dimension).

$\theta-2\theta$ X-ray diffraction scans and Laue X-ray diffraction were used to detect structure and the single-crystalline nature of the crystals [9]. The chemical composition was determined by electron probe micro analysis (EPMA). T_c of the single crystals was derived from the a.c. susceptibility measurements and $j_c(T)$ was obtained from the remanent magnetisation measured with a SQUID magnetometer [10].

The chemical composition of the single crystals is slightly different from the nominal one, which is summarised in Table I. An increase of the substituent in the single crystals compared with the nominal concentration is observed.

The X-ray diffraction patterns of the doped single crystals do not reveal any second phase. It was reported that for the Co doped samples the solubility limit is $x = 0.1$ [2,4-5]. Our doping level of Co is below this limit. For Ni doped Bi-2212 a solubility of $x = 0.02$ was reported for the polycrystalline samples [2]. Our result shows a solubility up to 0.05 for the Ni doped single crystals.

As shown in Fig. 1 the c-axis length decreases with the Ni as well as with the Co

TABLE I. Chemical composition of Co and Ni doped Bi-2212 single crystals measured by EPMA.

nominal	Bi	Sr	Ca	c u	M (Co/Ni)M/Cu ratio	
Ni 2%	2.00	1.91	1.00	2.02	0.04	2.0%
Ni 4%	2.00	1.96	0.93	2.01	0.10	5.0%
Co 1%	2.13	2.26	0.81	1.76	0.04	2.3%
Co 2%	2.10	2.18	0.90	1.76	0.07	4.0%
Co 5%	2.12	2.17	0.98	1.64	0.09	5.5%

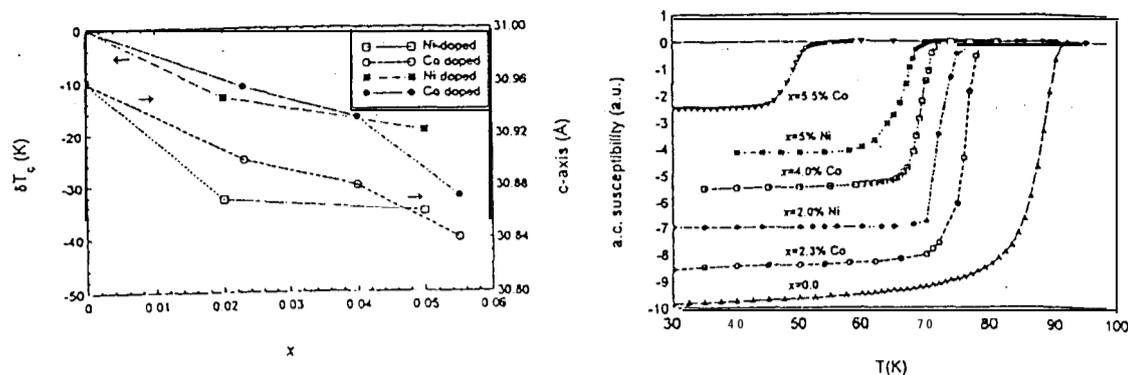


FIG. 1. The c-axis length (open data, right scale) and the change of the critical temperature (solid data, left scale) of the Co and Ni doped Bi-2212 single crystals versus the substituent concentration.

FIG. 2. a.c. susceptibility ($H_{ac} = 8$ Gauss, $f = 920$ Hz) of Co and Ni doped Bi-2212 single crystals.

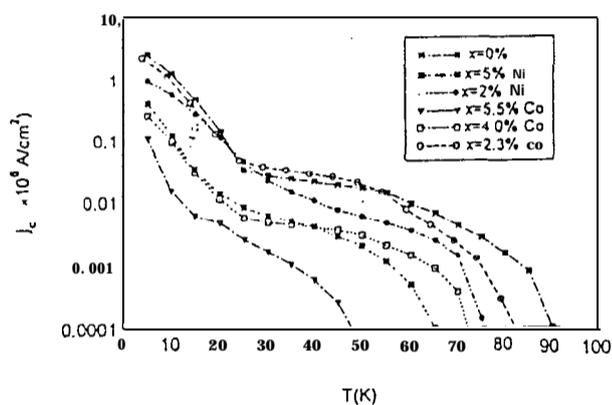


FIG. 3. Temperature dependence of $j_c(T)$ of the Co and Ni doped Bi-2212 single crystals in a semi-log plot. The kink of the curves is due to the transition of different pinning regimes (see text).

concentration. The decrease is more or less linear for the Co-doped samples, which seems not to be the case for the Ni-doped single crystals up to 5% Ni. The shrinking of the c-axis length can be related to the smaller ion size of the substituents ($r = 0.79$ Å for Cu^{2+} , 0.74 Å for Co^{2+} and 0.72 Å for Ni^{2+}).

The a.c. susceptibility data are shown in Fig. 2 with no sign of any second phase, in support of the X-ray diffraction data. The transition width (between 10% and 90% of the full AC field expulsion), is also almost the same (5-7 K) for all the samples. The T_c , defined as the onset temperature, decreases with the Co or Ni concentration, as given in Fig. 1.

The initial changing rate of T_c is about 5 K per percentage of the 3d-element concentration, in good agreement with the existing published data [2,4-6].

The $j_c(T)$ of the single crystals is shown in Fig. 3 with a semi-log plot. The $j_c(T=5\text{ K})$ decreases with the doping. A kink in the $j_c(T)$ curves is found for all the samples, which is typical for Bi-2212 crystals [10-11]. Regarding to the dimensionality of the vortices we note that the self-field induced by the critical current at 4.2 K is about 3-4 kG for our samples, which is in the 3D regime; and at $T \approx 30\text{ K}$, where the kink occurs, the self-field is about 50 G, which is very weak to break the flux lines to 2D pancakes. Metlushko et al. [11] identified this kink as a transition from individual/small-bundle flux pinning to large-flux-bundle collective pinning, which occurs when j_c drops to a critical value J_{cr} :

$$J_{cr} = j_0/\kappa^2$$

with j_0 the depairing current and κ the Ginzburg-Landau parameter. By using the available parameters for Bi-2212, one obtains a value of J_{cr} to be $10^4 - 10^5\text{ A/cm}^2$. In our experiments, for $x=0$, $x=2.3\%$ of Co and $x=2\%$ of Ni, J_{cr} is about $4 \times 10^4\text{ A/cm}^2$, which is indeed in the range of the theoretical value. However, for $x=4\%$, 5.5% of Co, and $x=5\%$ of Ni, the value of J_{cr} reduces to about $7 \times 10^3\text{ A/cm}^2$. This is in contrast with the results on Y-substituted $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+x}$ single crystals [12], for which J_{cr} is almost the same up to 28% Y, although $j_c(T=4.2\text{ K})$ decreases with the Y concentration. The explanation might be that the Y-substitution affects the pinning mainly by the decrease of the oxygen vacancies in the Cu-O planes; but the doping of the 3d elements mainly introduces cation impurities in the Cu-G planes that leads to a decrease of the coherent length ξ and an increase of κ [6], which reduces J_{cr} . In this case, we support the view that an impurity induced pair breaking, rather than an increase of the oxygen content, is the main cause for the depressing of T_c of the 3d-element substituted Bi-2212. Since the impurities of Y or 3d-elements themselves do not contribute to j_c , we conclude that the oxygen deficiencies in the Cu-O planes are the pinning centres in the Bi-2212 single crystals.

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References

- [1] T. E. Jones, P. M. Tambado, W. C. McGinnis, R. D. Boss, J. W. Schindler, and S. Oseroff, *Physica C* 162-164, 25 (1989).
- [2] A. Maeda, T. Yabe, S. Takebayashi, M. Hase, and K. Uchinokura, *Phys. Rev.* B41, 4112 (1990).
- [3] S. T. Lin, W. S. Chung, C. Y. Chou, and C. M. Lin, *J. Phys. Condens. Matter* 2, 8763 (1990).
- [4] P. Sumana Prabhhu, M. S. Ramachandra Rao, and G. V. Subba Rao, *Physica C* 211, 279 (1993).
- [5] M. Boekholt, Th. Eilmeier, L. Buschmann, M. Fleuster, and G. Giintherodt, *Physica C* 198, 33 (1992).
- [6] B. vom Hedt, W. Liseck, K. Westerholt, and H. Bach, *Phys. Rev.* B49, 9898 (1994).
- [7] G. D. Gu, K. Takamuku, N. Koshizuka, S. Tanaka, *J. Crystal Growth* 137, 472 (1994).
- [8] M. J. V. Menken, A. J. M. Winkelman, and A. A. Menosky, *J. Crystal Growth* 113, 9 (1991).
- [9] J. H. P. M. Emmen, S. K. J. Lenczowski, J. H. J. Dalderop, and V. A. M. Brabers, *J. of Crystal Growth* 118, 477 (1992).
- [10] D. Hu, W. Paul and J. Rhyner, *Physica C* 200, 359 (1992).
- [11] V. V. Metlushko, G. Giintherodt, V. V. Moshchalkov, and Y. Bruynseraede, *Europhys. Lett.* 26, 371 (1994).
- [12] D. Hu, V. Brabers, and W. J. M. de Jonge, *Physica C* 235, 951 (1994).