

# Superconducting and Transport Properties of (Bi-Pb)-Sr-Ca-Cu-O with Nano-Cr<sub>2</sub>O<sub>3</sub> Additions

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The effect of nano Cr<sub>2</sub>O<sub>3</sub> additions in (Bi, Pb)-Sr-Ca-Cu-O superconductors using the coprecipitation method is reported. Nano Cr<sub>2</sub>O<sub>3</sub> with 0.1, 0.3, 0.5, 0.7, and 1.0 wt.% were added to the (Bi, Pb)-Sr-Ca-Cu-O system. The critical temperature ( $T_c$ ) and transport critical current density ( $J_c$ ) were determined by the four-point probe technique. The phases in the samples were determined using the powder X-ray diffraction method. The microstructure was observed by a scanning electron microscope and the distribution of nano Cr<sub>2</sub>O<sub>3</sub> was determined by energy-dispersive X-ray analysis (EDX). The maximum  $T_c$  and  $J_c$  were observed for the sample with 0.1 wt.% nano Cr<sub>2</sub>O<sub>3</sub>. The variation in the  $J_c$  of all the samples was explained by the effective flux pinning by nano Cr<sub>2</sub>O<sub>3</sub> in the samples. Using the self-field approximation together with the dependence of  $J_c$  on temperature, the characteristic length ( $L_c$ ) associated with the pinning force was estimated to be approximately the same as the average grain size in all the samples.

**Key words:** Superconductor, nano Cr<sub>2</sub>O<sub>3</sub>, transport critical current density, self-field

## INTRODUCTION

Following the discovery of the Bi-Sr-Ca-Cu-O superconductor system,<sup>1</sup> worldwide research efforts to improve its superconducting properties have been actively undertaken. To enhance its current-carrying capacity, various methods have been employed, including introducing artificial flux pinning. The critical temperature,  $T_c$ , and critical current density,  $J_c$ , are found to increase with Gd substitution at the Sr site.<sup>2</sup> At 77 K, the self-field  $J_c$  of the samples with added Nd was found to be much higher than the undoped one.<sup>3</sup> In particular a small amount of chromium oxide doping improves the flux pinning, with the effective pinning center due to Cr substitution for Cu, while excessive Cr-ion doping degrades the superconductivity of Bi<sub>1.6</sub>Pb<sub>0.4</sub>Sr<sub>2</sub>Ca<sub>2</sub>Cu<sub>3</sub>O<sub>10</sub> (2223).<sup>4</sup> The  $T_c$  of Cr-doped Bi-Sr-Ca-Cu-O decreased due to the decrease of the hole concen-

tration through substitution of Cr<sup>3+</sup> for Cu<sup>2+</sup>. The substitution also causes appreciable change in the normal-state conductivity.<sup>5</sup> Proper Cr doping seems to be a convenient and effective method to introduce artificial defects into the Bi2223 system as pinning centers.<sup>6</sup>

To the best of our knowledge, nano Cr<sub>2</sub>O<sub>3</sub> additions in Bi-Sr-Ca-Cu-O superconductors have not yet been reported. The magnetic properties of Cr<sub>2</sub>O<sub>3</sub> nanoparticles have been reported to show the presence of a net magnetic moment at the surface due to the large surface-to-volume ratio which modifies the classical behavior expected for bulk antiferromagnetic particles.<sup>7</sup> Hence, it is interesting to investigate further the effect of nano Cr<sub>2</sub>O<sub>3</sub> in the Bi-Sr-Ca-Cu-O system. In this paper, we report the effect of nano Cr<sub>2</sub>O<sub>3</sub> additions in Bi-Sr-Ca-Cu-O particularly with respect to  $T_c$  and  $J_c$ . The self-field approximation was employed to estimate the relationship between the characteristic length associated with the pinning force and the grain size of the samples.

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## METHODOLOGY

The samples were prepared from ultrafine superconductor powders made using the coprecipitation method described elsewhere.<sup>8</sup> Nano Cr<sub>2</sub>O<sub>3</sub> with an average size 6.5 nm (from Aldrich) with amounts of 0.1, 0.3, 0.5, 0.7, and 1.0 wt.% were added to the powder. Samples were pressed into pellets with 13 mm diameter and 2 mm thickness and sintered at 850°C for 48 h.

The electrical resistance-temperature measurements were carried out by the four-point probe technique in conjunction with a CTI cryogenics closed-cycle refrigerator (Model 22). The critical current density was measured on bar-shape samples between 30 K and 77 K using the 1  $\mu$ V/cm criterion.

Powder X-ray diffraction patterns were recorded using a Siemens D 5000 diffractometer with CuK <sub>$\alpha$</sub>  radiation. The volume fraction of the 2223 and (Bi<sub>1.6</sub>Pb<sub>0.4</sub>)Sr<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> (2212) phases was estimated by assuming that the amounts of these phases was proportional to the strongest diffraction line of each phase.<sup>9</sup> The microstructures were determined from scanning electron micrographs (SEM). The distribution of nano Cr<sub>2</sub>O<sub>3</sub> was investigated using energy-dispersive X-ray analysis (EDX). A Philips transmission electron microscope (TEM) model CM12 was used to determine the size of the nano Cr<sub>2</sub>O<sub>3</sub>.

## RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the samples. The samples consist of 2223 as the major phase and 2212 as the minor phase. The volume fraction can be calculated from the XRD pattern of the highest peak of the 2223 and the highest peak (\*) of the 2212 phase.<sup>9</sup> The volume fraction of the 2223 phase for

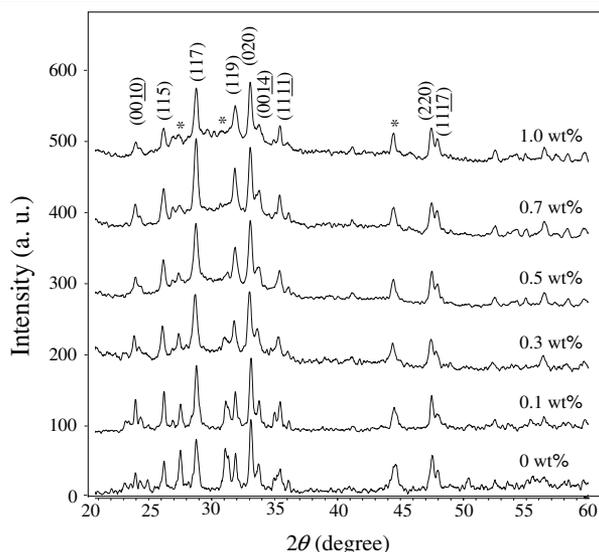


Fig. 1. XRD patterns of the undoped sample and with added nano Cr<sub>2</sub>O<sub>3</sub>. (\*) denotes the Bi2212 phase.

the sample with 0.1 wt.% nano Cr<sub>2</sub>O<sub>3</sub> shows the highest percentage (71%). There is not much difference in the volume fraction with further additions of nano Cr<sub>2</sub>O<sub>3</sub>.

The temperature where the resistance begins to show a sudden drop ( $T_{c-onset}$ ), the zero-resistance temperature ( $T_{c-zero}$ ), the percentage of the 2223 and 2212 phases, and the distribution of nano Cr<sub>2</sub>O<sub>3</sub> are shown in Table I. Figure 2 shows the curve of electrical resistance versus temperature for the samples. Figure 3 shows  $T_{c-onset}$  and  $T_{c-zero}$  versus nano Cr<sub>2</sub>O<sub>3</sub> content. The  $T_{c-onset}$  for the 0.1 wt.% nano Cr<sub>2</sub>O<sub>3</sub> is the highest (111 K), whereas the undoped sample exhibited a  $T_{c-onset}$  of 108 K. When the amount of nano Cr<sub>2</sub>O<sub>3</sub> was increased from 0.3 wt.% to 1.0 wt.%,  $T_{c-onset}$  decreased from 110 K to 100 K, whereas  $T_{c-zero}$  decreased from 97 K to 81 K. The results shows that the highest percentage of the 2223 phase gives the highest  $T_c$ . The anomalous  $T_{c-zero}$  for the  $x = 0.5$  wt.% sample may be due to inhomogeneity in the sample, which can affect the

Table I.  $T_{c-onset}$ ,  $T_{c-zero}$ , Percentages of the 2223 and 2212 Phases and Distribution of Nano Cr<sub>2</sub>O<sub>3</sub> (in the 0.1, 0.5, and 1.0 wt.% Added Samples)

$x$ (wt.%)	$T_{c-onset}$ ( $\pm 1$ K)	$T_{c-zero}$ ( $\pm 1$ K)	Volume Fraction (%)		Distribution of Nano Cr <sub>2</sub> O <sub>3</sub> (count/ $\mu$ m <sup>2</sup> )
			2223	2212	
0	108	98	62	38	0.09
0.1	111	101	71	29	
0.3	110	97	69	31	0.29
0.5	108	97	68	32	
0.7	105	88	68	32	0.57
1.0	100	81	67	33	

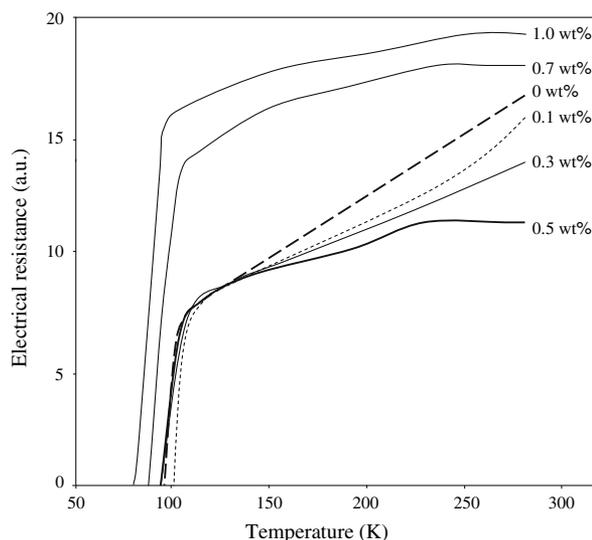


Fig. 2. Electrical resistance versus temperature for Bi-Sr-Ca-Cu-O with nano Cr<sub>2</sub>O<sub>3</sub> added at 0, 0.1, 0.3, 0.5, 0.7, and 1.0 wt.%.

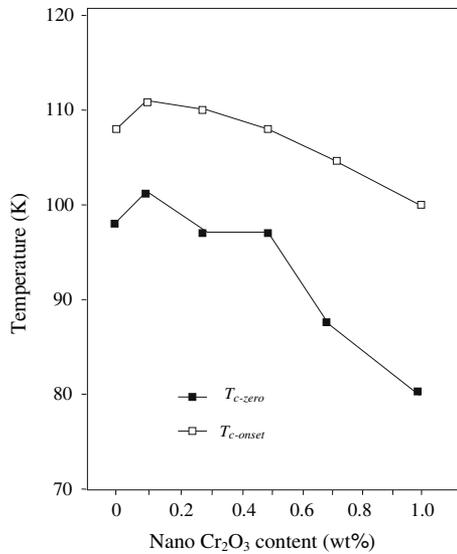


Fig. 3.  $T_{c\text{-onset}}$  and  $T_{c\text{-zero}}$  versus nano  $\text{Cr}_2\text{O}_3$  content (solid lines are guides to the eye).

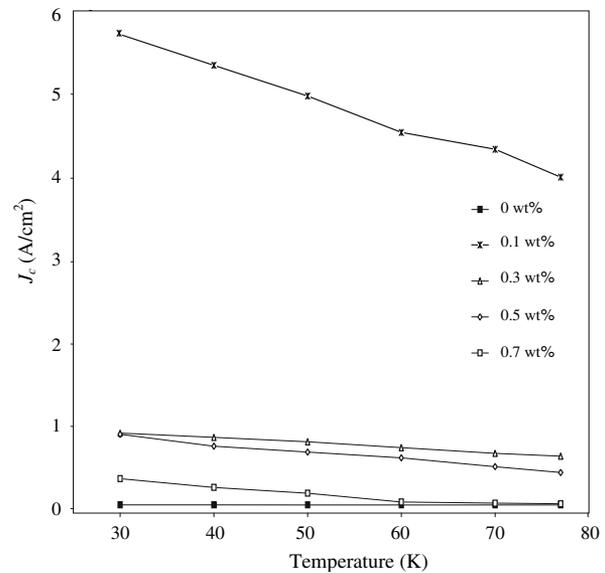


Fig. 4. Temperature dependence of  $J_c$  in the pure and nano  $\text{Cr}_2\text{O}_3$  addition samples (solid lines are guides to the eye).

transport properties in this type of materials (see, for example, Refs. 10 and 11).

Further addition of nano  $\text{Cr}_2\text{O}_3$  up to 1.0 wt.% decreases both  $T_{c\text{-onset}}$  and  $T_{c\text{-zero}}$  of the samples. The decrease in the critical temperature is caused by overdoping of nano  $\text{Cr}_2\text{O}_3$  to the 2223 system. Barik et al.<sup>5</sup> reported that suppression of  $T_c$  with increasing Cr concentration supports the pair-breaking mechanism. Hu et al.<sup>6</sup> reported that a small amount of  $\text{CrO}_3$  addition improved flux pinning, with effective pinning centers due to Cr substitution for Cu, while excessive Cr-ion doping degraded the superconductivity of Bi2223.

Figure 4 shows the temperature dependence of  $J_c$  for the pure and added samples. Overall,  $J_c$  decreases with increasing temperature as a consequence of thermally activated flux creep. For the undoped sample, the  $J_c$  at 77 K is about 30 mA/cm<sup>2</sup>. The existence of the 2212 phase in the undoped sample suppresses the current-carrying capability due to the weak-link problem. The lower  $J_c$  may be caused by the presence of an impurity phase that does not act as flux pinning centers. The  $J_c$  of the sample increased to 3,980 mA/cm<sup>2</sup> for the 0.1 wt.% nano  $\text{Cr}_2\text{O}_3$  samples.  $J_c$  decreased when higher amounts of nano  $\text{Cr}_2\text{O}_3$  were added. There was an increase in  $J_c$  for all the nano  $\text{Cr}_2\text{O}_3$ -added samples compared to the undoped sample. The addition of nano  $\text{Cr}_2\text{O}_3$  can improve the intergrain connectivity. The nanoparticles may reside at the grain boundaries or go into the grains, which plays a role in the effective pinning centers and leads to the increase of  $J_c$ . In other words, the flux pinning strength of the added samples is significantly enhanced compared to the undoped sample.

Figure 5 shows SEM micrographs for the samples with 0.1, 0.5, and 1.0 wt.% nano  $\text{Cr}_2\text{O}_3$ . All of

the samples show a similar grain alignment with elongated plate-like grains with a length of about 5  $\mu\text{m}$  or less. The distribution of  $\text{Cr}_2\text{O}_3$  is shown by the white dots. The distribution (number density) of nano  $\text{Cr}_2\text{O}_3$  was calculated by counting the number of dots in the SEM micrograph and dividing by the total area. The distribution of nano  $\text{Cr}_2\text{O}_3$  increases (as expected) from 0.09 count/ $\mu\text{m}^2$  for the 0.1 wt.% sample, to 0.57 count/ $\mu\text{m}^2$  for the 1.0 wt.% sample.

The current-carrying capability is directly related to the bulk pinning force density  $F_p$ . For spherical pinning centers with radius  $R$ , Ullmaier showed that  $F_p \approx F_p[B_c(T)]^m$ , where  $m = 3/2$  for  $R > \xi$  and  $m = 5/2$  for  $R < \xi$ , where  $\xi$  is the coherence length.<sup>12</sup> From the TEM results (Fig. 6), the average size of  $\text{Cr}_2\text{O}_3$  is about 6.5 nm. The coherence length of the 2223 system is around 2.9 nm,<sup>13</sup> i.e., the diameter of the pinning center is larger than the coherence length ( $R > \xi$ ), consistent with  $m = 3/2$ . This is also consistent with the self-field effect in the curve of  $J_c$  versus temperature.<sup>14</sup> Using the self-field approximation together with the  $J_c$  dependence on  $T$ , it is observed that between 30 K and 77 K the characteristic length ( $L_c$ ) associated with the pinning force is approximately the same as the average grain size<sup>14,15</sup> in all the samples. Figure 5b–d shows that the distance between nearest the nano  $\text{Cr}_2\text{O}_3$  particles is generally smaller than the average plate size of Bi-Sr-Ca-Cu-O in all the samples. This indicates that not all the  $\text{Cr}_2\text{O}_3$  act as pinning centers, especially for samples with more than 0.1 wt.%  $\text{Cr}_2\text{O}_3$ , which coincides with the abrupt decrease in  $J_c$ .

In conclusion, nano  $\text{Cr}_2\text{O}_3$  addition to Bi-Sr-Ca-Cu-O can improve the superconducting properties of the samples. The sample with 0.1 wt.% addition had

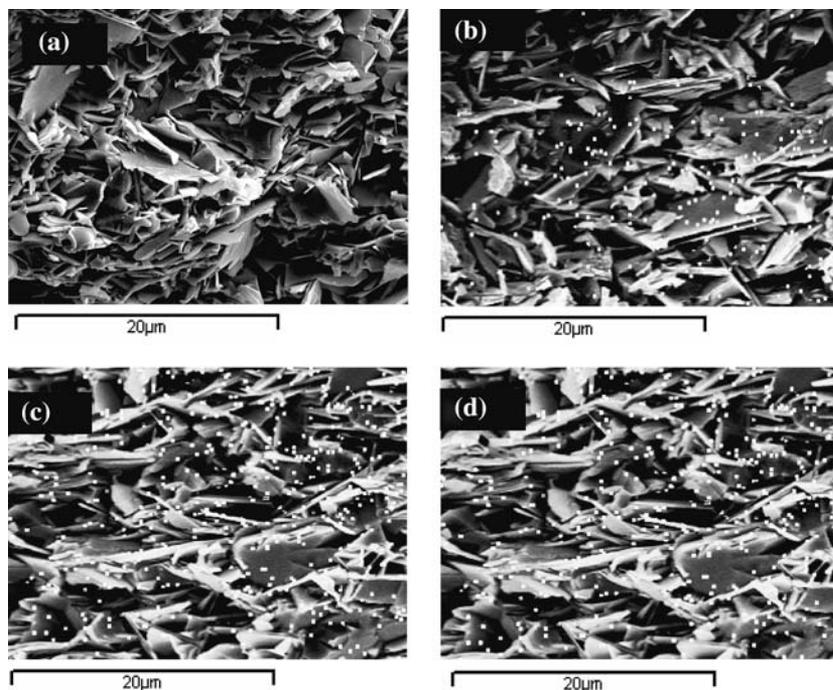


Fig. 5. SEM micrographs of the samples with (a) 0 wt.%, (b) 0.1 wt.%, (c) 0.5 wt.%, and (d) 1.0 wt.% Cr<sub>2</sub>O<sub>3</sub> addition. The distribution of nano Cr<sub>2</sub>O<sub>3</sub> is indicated by the white dots.

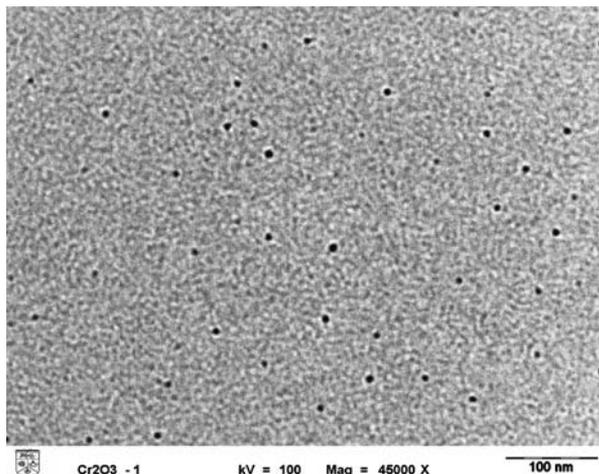


Fig. 6. TEM image with Cr<sub>2</sub>O<sub>3</sub> shown as black spots.

the highest  $T_{c-onset}$  and  $T_{c-zero}$ . The same sample also exhibited the highest volume fraction of the 2223 phase (71%). These results show that an appropriate amount of nano Cr<sub>2</sub>O<sub>3</sub> can improve the superconducting properties of the Bi-based samples, while excessive nano Cr<sub>2</sub>O<sub>3</sub> addition leads to degradation of the superconductivity of Bi2223.

### CONCLUSIONS

The  $J_c$  of all the samples increased with the addition of nano Cr<sub>2</sub>O<sub>3</sub>. Nano Cr<sub>2</sub>O<sub>3</sub> additions at

very small percentages in the Bi-Sr-Ca-Cu-O system enhanced the transport critical current density.

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