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ORIGINAL PAPER

Variation of Mechanical Properties of Cr Doped Bi-2212 Superconductors

M. Dogruer · G. Yildirim · O. Ozturk · I. Belenli · C. Terzioglu

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Abstract This study shows the influence of Cr inclusions on the mechanical properties of $Bi_{1.8}Sr_{2.0}Cr_xCa_{1.1}Cu_{2.1}O_y$ (Bi-2212) superconducting samples ($x = 0$, 0.1, 0.3, 0.5, 0.7, and 1) prepared by conventional solid-state reaction route with the aid of the microhardness (H_v) measurements. Moreover, some characteristics such as Vickers microhardness, Young's (elastic) modulus (E) and yield strength (Y), being responsible for the potential technological and industrial applications, are theoretically evaluated from the microhardness curves belonging to the samples and compared with each other. It is found that the load dependent microhardness values decrease nonlinearly as the applied load enhances until 2 N beyond, which the curves shift to the saturation region, confirming that all the samples exhibit the indentation size effect (ISE) nature. Further, the elastic modulus and yield strength values observed reduce with the enhancement of the applied load and Cr inclusions in the Bi-2212 matrix. The experimental findings are also analyzed by Meyer's law, proportional sample resistance model (*PSR*), modified proportional sample resistance model (*MPRS*), elastic/plastic deformation model (*EPD*), and Hays–Kendall (*HK*) approach. According to the results obtained, the load independent microhardness values calculated by EPD, PSR, and MPSR models are far from the values of the plateau region; however, the HK approach is the most suitable model for the microhardness calculations of the samples prepared in this study.

Keywords $Bi_{1.8}Sr_{2.0}Cr_xCa_{1.1}Cu_{2.1}O_y$ · H_v · H_{PSR} · H_{MPSR} · H_{EPD} · H_{HK}

1 Introduction

Although Bi-based high-temperature superconductors play a significant role for the potential technological and industrial applications [1–3] owing to the their remarkable smaller power losses, high current and magnetic field carrying capacity, optical and electronic properties [4, 5], the mechanical properties limit their applications due to the brittleness nature of the high-temperature superconducting ceramics. Thus, for several years, the researchers have endeavored to improve the mechanical properties including the hardness, yield strength, elasticity, ductility, fracture toughness, and brittleness index with the aid of the chemical doping, substitution, transition metal evaporation, and changing preparation conditions [6, 7]. As received, among the methods, the chemical doping is one of the most preferred methods [8, 9] because of the simple production mechanism [10–13].

In this paper, we examine the role of the mechanical properties of Cr doped Bi 2212 ceramics via Vickers microhardness (H_v) measurements. The Vickers hardness, Young's modulus, and yield strength values are deduced from the H_v measurements. The results of the microhardness measurements are also analyzed by different available models such as Meyer's law, PSR, MPSR, EPD, and HK model.

M. Dogruer · G. Yildirim · I. Belenli · C. Terzioglu (✉)
Department of Physics, Abant Izzet Baysal University, 14280 Bolu, Turkey
e-mail: terzioglu_c@ibu.edu.tr

G. Yildirim
Department of Mechanical Engineering, Abant Izzet Baysal University, 14280 Bolu, Turkey

O. Ozturk
Department of Physics, Kastamonu University, 37100 Kastamonu, Turkey

2 Experimental Details

In previous work [14], we performed the dc resistivity (ρ–T), X-ray analysis (*XRD*), scanning electron microscopy (*SEM*), and energy dispersive spectroscopy (*EDS*) measurements belonging to the Cr doped Bi-2212 superconducting ceramics. Further, the change of the flux pinning mechanism properties in the applied magnetic fields range of 0–7 T was investigated clearly [15]. One can see the results with the sample preparation procedure in [14] in detail. In the present study, the effect of Cr addition level on the mechanical properties of the Bi-2212 superconductors is examined by way of Vickers microhardness (H_v) measurements, which are conducted in air using a SHIMADZU HVM-2 model digital microhardness tester. The applied load is varied from 0.245 to 2.940 N for a loading time of 10 seconds and accuracy in the determination of indentation diagonals is measured to be ±0.1 µm. The indenter is also pressed on the different locations on the specimen surface to avoid surface effects and work hardening. Here, the undoped sample is reported as Cr0 whereas the superconductor samples produced with different Cr concentration such as 0.1, 0.3, 0.5, 0.7, and 1 will be herein after presented as Cr1, Cr2, Cr3, Cr4, and Cr5, respectively.

3 Results and Discussion

We have examined the electrical, physical, structural and superconducting properties of the Cr doped Bi-2212 samples in [14] and discussed that the zero-resistivity transition temperature reduces with the enhancement of Cr additive in Bi-2212 material. Besides, XRD examinations illustrated that the lattice constants a increases whereas the c parameter decreases with the Cr addition. Additionally, SEM results demonstrated that the surface morphology and grain connectivity are obtained to degrade, and the grain sizes of the samples studied are found to reduce with the increase of the Cr addition. In addition, EDS measurements pointed out that the Sr and Cu compositions in the samples compared to other element compositions gradually decrease up to maximum content. Based on the result, the Cr atoms are determined to enter into the crystal structure by replacing Sr and Cu atoms, which causes to degrade the structural and superconducting properties of the samples studied. Similarly, we displayed that the flux pinning and activation energy values deteriorate with the Cr concentration level in the Bi-2212 system [15]. In the current work, the change of mechanical properties with the Cr doped Bi-2212 material is studied via Vickers microhardness (H_v) measurements. We also use a number of models to define the ISE nature.

3.1 Microhardness and Modeling

In order to estimate the crucial change in the mechanical performances of $Bi_{1.8}Sr_{2.0}Cr_xCa_{1.1}Cu_{2.1}O_y$ superconductor samples, we measure the diagonal length as a function of test load. The Vickers microhardness (H_v) values can be estimated according to the following equation:

$$H_v = 1854.4\left(\frac{F}{d^2}\right) \quad (1)$$

where $F(N)$ is the applied load and d (µm) is the diagonal length of the indentation. The calculated load dependent microhardness values for different applied loads (0.245, 0.490, 0.980, 1.960, and 2.940 N) are gathered in Table 1. As can be seen, the microhardness values for all the samples depend on the applied loads. It is apparent from the table that the H_v values decrease with applied load for all samples. The variation of Vickers microhardness with the applied loads for pure and Cr inclusions in Bi-2212 materials are illustrated in Fig. 1. As seen from the figure that all samples exhibit the ISE behavior being attributed to the fact that the H_v values reduce nonlinearly as the applied load increases until 2.0 N after this point, the curves shift to the plateau (saturation) region. This may lead to the contribution of the grain boundary weak-links, specimen cracking/porosity, disorder, impurity phases, and irregular grain orientation distribution [16].

Additionally, the Young's (elastic) modulus (E) and yield strength (Y) can be defined by the equations:

$$E = 81.9635 H_v \quad (2)$$

$$Y \approx \frac{H_v}{3} \quad (3)$$

The results calculated are summarized in Table 1, as seen from the table that all the values obtained are associated with

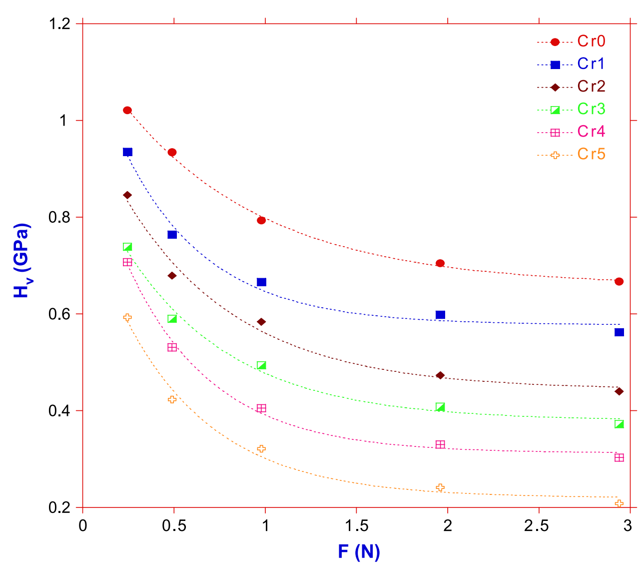

Fig. 1 Variation of microhardness value with applied load for all samples

Table 1 The calculated load dependent H_v, E, and Y for the samples produced

Samples	d (μm)	H_v (GPa)	E (GPa)	Y (GPa)
Cr0	21.09	1.021	83.684	0.340
	31.18	0.934	76.553	0.311
	47.85	0.793	64.997	0.264
	71.76	0.705	57.784	0.235
	90.38	0.667	54.669	0.222
Cr1	22.04	0.935	76.635	0.312
	34.47	0.764	62.620	0.254
	52.23	0.666	54.587	0.222
	77.95	0.598	49.014	0.199
	98.41	0.562	46.063	0.187
Cr2	23.17	0.846	69.341	0.282
	36.56	0.679	55.653	0.226
	55.77	0.584	47.866	0.194
	87.61	0.473	38.7687	0.157
	111.2	0.440	36.063	0.146
Cr3	24.79	0.739	60.571	0.246
	39.23	0.590	48.358	0.196
	60.62	0.494	40.489	0.164
	94.36	0.408	33.441	0.136
	121.04	0.372	30.490	0.124
Cr4	25.34	0.707	57.948	0.235
	41.35	0.531	43.522	0.177
	66.98	0.405	33.195	0.135
	104.93	0.330	27.047	0.110
	134.01	0.303	24.834	0.101
Cr5	27.67	0.593	48.604	0.197
	46.32	0.423	34.670	0.141
	75.16	0.321	26.310	0.107
	122.65	0.241	19.753	0.080
	161.64	0.208	17.048	0.069

both the applied load and Cr inclusions. Elastic modulus and yield strength values are observed to reduce with the applied load for all the samples showing the ISE nature. Besides, we use 5 different models such as Meyer's law, the PSR model, MPSR model, EPD model, and HK approach to calculate the load independent microhardness values and describe the ISE feature.

3.1.1 *Meyer's Law*

In order to explain the ISE of the samples, Meyer's law can be described by the equation:

$$F = A_1 d^n \qquad (4)$$

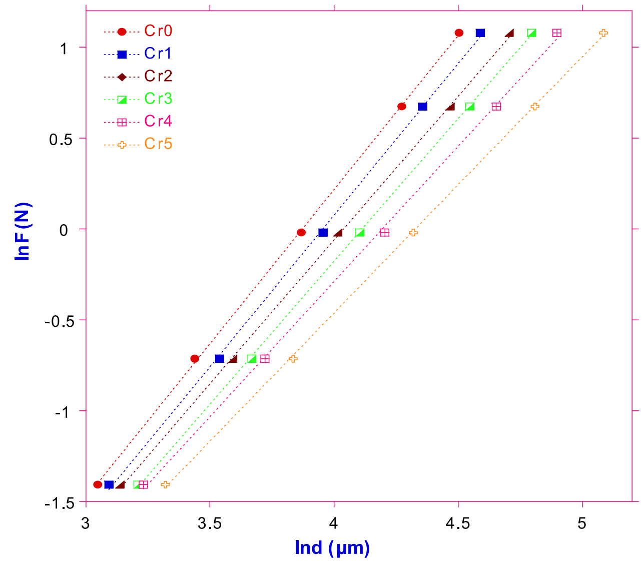

Fig. 2 Variation of applied load ln F with diagonal ln d for all samples

where the power n is the Meyer number and A_1 denotes the standard microhardness constants. The plots of ln F versus ln d for all the samples are illustrated in Fig. 2. The slope of the graph is proportional to n and A_1 presents the vertical intercept of the curve. The values of n and A_1 are gathered in Table 2. Additionally, the n values are found to be less than 2 for all samples on account of the ISE nature.

3.1.2 *PSR Model*

For the mechanical characterizations of the samples studied in this work, the ISE nature can be defined by means of the following equation:

$$\frac{F}{d} = \alpha + \beta d \qquad (5)$$

where α is the surface energy and β denotes hardness constant. The load independent microhardness value is computed by use of equation:

$$H_{PSR} = 1854.4\beta \qquad (6)$$

Figure 3 visualized F/d versus the d graph for all the samples. The parameters of α and β are given in Table 2, as seen from the table that the α values are positive for Cr inclusions inserted in the Bi-2212 samples, illustrating that all samples reveal the ISE nature. Additionally, the calculated H_{PSR} are gathered in Table 3. It is clear from the table that the load independent microhardness values computed by PSR model are far from the load dependent hardness value (plateau region). Therefore, it is obvious that the PSR model is inadequate for the explanation of the real microhardness value of the Cr addition in Bi-2212 systems.

Table 2 The calculated parameters according to different models for Bi-2223 system

Samples	Meyer's law		PSR model		MPSR model			EPD model		HK model	
	$A_1 \times 10^{-3}$ (N/μm^2)	n	$\alpha \times 10^{-3}$ (N/μm)	$\beta \times 10^{-4}$ (N/μm^2)	W_1 (N)	A_2 (N/μm)	$A_3 \times 10^{-4}$ (N/μm^2)	d_e (μm)	$A_4 \times 10^{-2}$ (N/μm^2)	W_2 (N)	$A_5 \times 10^{-4}$ (N/μm^2)
Cr0	1.401	1.69	5.993	2.962	−0.0555	0.0088	2.6879	0.1437	1.7468	0.1449	3.4599
Cr1	1.379	1.66	5.758	2.466	−0.0326	0.0072	2.3358	0.1486	1.5982	0.1454	2.9202
Cr2	1.673	1.58	6.913	1.775	−0.0632	0.0097	1.5497	0.1951	1.3757	0.1967	2.2504
Cr3	1.573	1.56	6.618	1.485	−0.0795	0.0098	1.2493	0.2015	1.2621	0.2050	1.9023
Cr4	1.955	1.48	7.065	1.112	−0.0094	0.0074	1.0829	0.2299	1.1138	0.2222	1.5371
Cr5	2.234	1.40	7.352	0.689	−0.0802	0.0100	0.5346	0.2756	0.9046	0.2812	1.0474

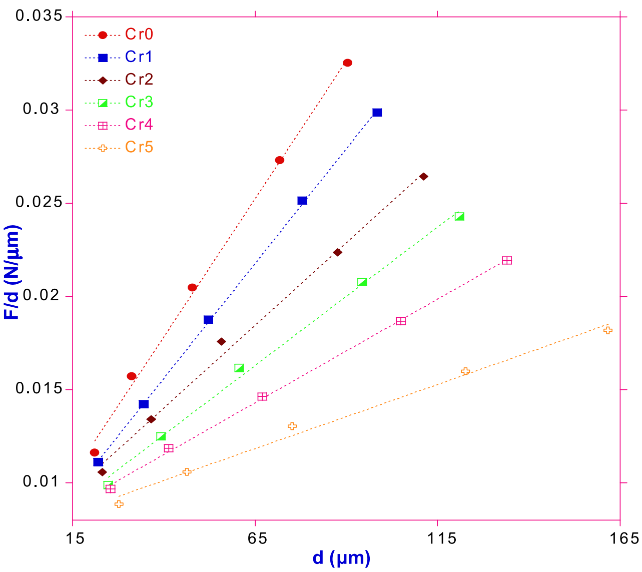

Fig. 3 Plots of F/d versus d for the samples studied

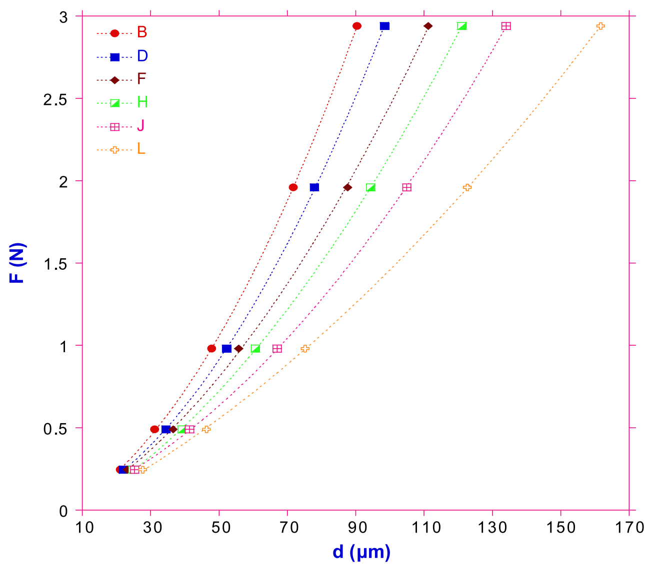

Fig. 4 Variation of the applied load with the indentation diagonal length for all samples

Table 3 The results of calculated values of H_v, H_{PSR}, H_{MPSR}, H_{EPD}, and H_{HK} approach

Samples	H_{MPRS} (GPa)	H_{PSR} (GPa)	H_{EPD} (GPa)	H_{HK} (GPa)	H_v (GPa)
Cr0	0.498	0.549	0.565	0.641	0.667–0.705
Cr1	0.433	0.457	0.473	0.541	0.562–0.568
Cr2	0.287	0.329	0.350	0.417	0.440–0.473
Cr3	0.231	0.275	2953	0.352	0.372–0.408
Cr4	0.200	0.206	0.230	0.285	0.303–0.330
Cr5	0.099	0.127	0.151	0.194	0.208–0.241

3.1.3 MPSR Model

The modified proportional specimen resistance model has proposed examining the ISE behavior. This model can be analyzed by means of the equation:

$$F = W_1 + A_2 d + A_3 d^2 \qquad (7)$$

where W_1 is the minimum applied load to generate an indentation, A_2 and A_3 are related to the dissipation energies to create a new surface of a unit area and produce the permanent deformation of a unit volume. Comparisons made between applied loads and indentation diagonal lengths with regard to Cr doped Bi-2212 superconductor are depicted in Fig. 4. The calculated values of W_1, A_2, and A_3 are given in Table 2. Further, using the MPSR model, the load independent hardness values are defined as

$$H_{MPSR} = 1854.4 A_3 \qquad (8)$$

The parameters of H_{MPRS} found for all the samples are summarized in Table 3. It is apparent from the table that the H_{MPRS} values computed by way of the MPSR model are also far from the values of the H_v.

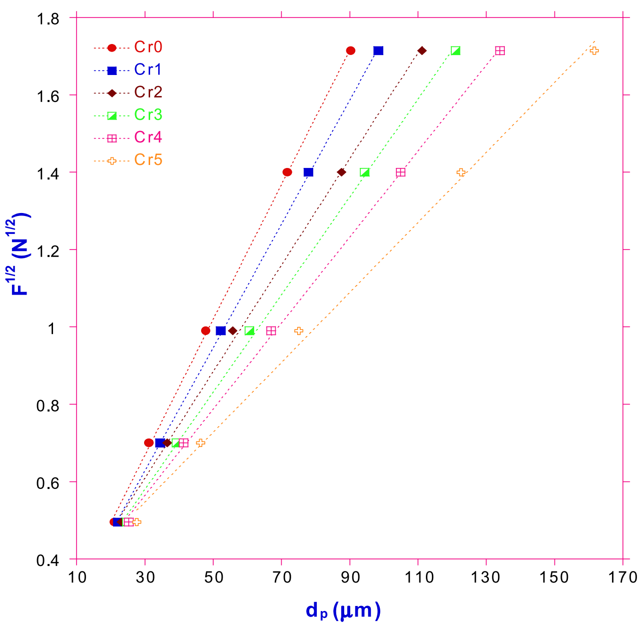

Fig. 5 Plots of square root of applied loads versus diagonal length for all samples

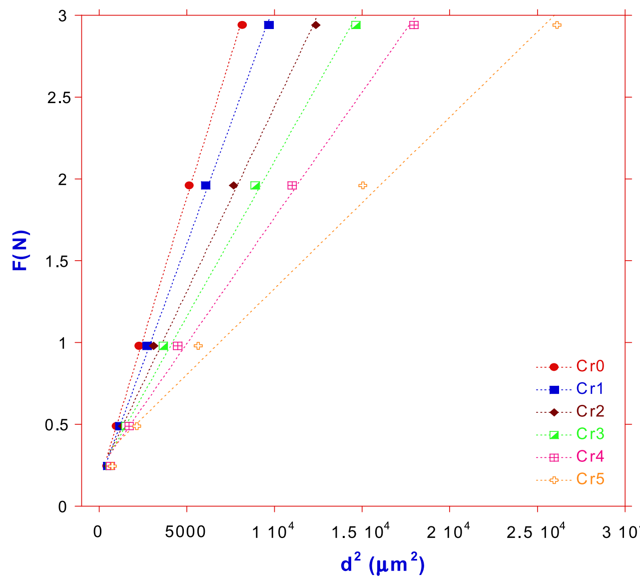

Fig. 6 Applied load versus the square of the impression length for the samples prepared

3.1.4 EPD Model

The dependence of indentation size on the applied load is computed by use of the equation given below:

$$F = A_4(d_e + d_p)^2 \tag{9}$$

where A_4 is the hardness constant, and elastic deformation (d_e) is related to (d_p) plastic deformation. The result of the A_4 and d_e given in Table 2 determined from the linear graphs of $F^{1/2}$ versus d_p for the $Bi_{1.8}Sr_{2.0}Cr_xCa_{1.1}Cu_{2.1}O_y$ superconductors (Fig. 5). It is visible from the table that the d_e is observed to be positive for the undoped and Cr addition in the Bi-2212 system illustrating the ISE feature. Moreover, the load independent microhardness value (H_{EPD}) can be calculated by the following formula:

$$H_{EPD} = 1854.4A_4 \tag{10}$$

One can see from Table 3 that the H_{EPD} values reduce with increment Cr content in the Bi-2212 materials. Additionally, it is apparent from the table that the EPD model is insufficient for the determination of the origin microhardness value.

3.1.5 HK Approach

Hays and Kendall (*HK*) [17] studied that there is a minimum test load W_2, which is essential to start the plastic deformation. Elastic deformation is only obtained when the W_2 is not exceeded with applied load. Hence, the experimentally measured indentation size is proportional to an effective load $F_{eff} = F - W_2$ instead of the applied load and obtained by the equation:

$$F - W_2 = A_5d^2 \tag{11}$$

where A_5 is the microhardness constant. The load independent microhardness values (H_{HK}) can be calculated by means of the following formula:

$$H_{HK} = 1854.4A_5 \tag{12}$$

Figure 6 displays F versus the d^2 graph for all the ceramics produced. The A_5 and W_2 parameters are deduced from the figure (Table 2). One can see from the table that the values of W_2 are positive for all samples presenting ISE nature. This may be attributed to the fact that the applied load is sufficient to produce both elastic and plastic deformation in the material, as can be seen from Table 3 that the H_{HK} values calculated from Hays and Kendall approach are closer to load dependent microhardness values (plateau region) when compared to other models. Thus, the HK approach is the most suitable model to define the mechanical properties of the samples.

4 Conclusions

In the present work, the effect of Cr addition on the mechanical properties of $Bi_{1.8}Sr_{2.0}Cr_xCa_{1.1}Cu_{2.1}O_y$ superconductor samples prepared by the standard solid-state reaction method with $x = 0$, 0.1, 0.3, 0.5, 0.7, and 1 is analyzed via the microhardness measurements. Additionally, the Vickers microhardness, elastic modulus and yield strength values are deduced from the measurements. The results observed show that the Vickers hardness, Young's modulus and yield strength values reduce with the increment in the applied load for the Bi-2212 superconducting ceramics. It is another interesting point that the Cr addition level leads to decrease considerably the characteristics given above due to the enhancement of the grain boundary weak-links, specimen cracking/porosity, disorder, impurity phases, and irregular grain orientation distribution. Besides, the experimental results of the microhardness measurements are studied by five different standard methods such as Meyer's law, PSR, MPSR, EPD, and HK approaches. Based on the findings obtained, all the Bi-2212 superconductors studied in this work display the ISE behavior. Furthermore, the PSR, MPSR, and EPD models fail to explain the mechanical properties of the samples; on the other hand, the HK approach is found to be the best fitted in terms of the origin microhardness values. To sum up, the HK approach is observed to be the most successful to describe the mechanical properties for all the samples.

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