

The influence of cooling rates on microstructure and mechanical properties of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductors

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Abstract. We investigated the effect of cooling rates on the microstructure and mechanical properties of $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductors prepared by standard solid state reaction methods. The samples were annealed under identical condition and cooled with different cooling rates. The investigations consisted of Vickers microhardness, SEM and XRD measurements. XRD examination of the samples showed that high percentage of Bi-2212 phase was observed and low- T_c phase increased with increasing the cooling rates. From SEM analysis, flake-like grains were more pronounced with increasing cooling rates. The indentation load versus diagonal length of the samples under different indentation loads in the range of 0.245-2.940 N were presented. We calculated Vickers hardness, Young's modulus, yield strength, fracture toughness values. These mechanical properties of the samples were found to be load and cooling rate dependent. In addition, we calculated the load independent microhardness, Young's modulus, and yield strength and fracture toughness of the samples using different models. The possible reasons for the observed changes in microstructure and mechanical properties of the samples due to cooling rates were discussed.

1. Introduction

BSCCO superconductor is one of the most interesting nominate material for technological applications [1]. Despite the potential advantages of this material compared with other superconductors (a lesser

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tendency to react with water or carbon dioxide, no need for special annealing in oxygen), it is often limited by its poor mechanical performance.

Variations in superconducting characteristics of pure and doped BiPbSrCaCuO reported by different research groups are often ascribed to different sintering conditions [2-4]. To find optimum preparation conditions for pure samples several studies have investigated the influence of cooling effect such as lattice parameters, critical temperature and volume fraction [5,6].

The mechanical properties of bulk BSCCO superconductor, as reported in the literature, can be summarized as low elastic modulus [7,8] low yield stress [9] and high degree of brittleness. However, Vickers microhardness indentation testing is a useful tool to probe the mechanical properties of these brittle materials because the requirement for large specimens is relaxed. Vickers indentation measurement of BSCCO superconductors have been reported by Jie Luo et al [10]. Veerinder et al. reported the results of Vickers microhardness of the $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$ superconductor at different loads [11].

It is generally known that cooling rates plays very important role as well as chemical doping in high- T_c superconductor materials. On the other hand, cooling rates are also very important for improving superconducting, microstructure and mechanical properties. It is useful to observe the variation both the microstructure and mechanical properties.

In this paper, we report the influence of the cooling rate on the microstructure and mechanical properties of bulk BiPbSrCaCuO samples. We prepared three different samples, via cooling in liquid nitrogen (fast quench), air (quench) and furnace (unquenched).

2. Experimental details

The samples were prepared with the help of the standard solid-state reaction method. The starting materials consisted of mixture of oxides (Bi_2O_3 , Pb_3O_4 , and CuO) and carbonates (SrCO_3 , CaCO_3) with a nominal composition $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$. The reaction mixture was calcinated at 800°C for 24 h. This sample cooled to room temperature to grind. The resulting powders were then pressed into pellets at the pressure of 300 MPa. The pellets were sintered in air 832°C for 120 h and then cooled. Samples were prepared way to different cooling. First group sample heated and cooled in furnace (NC) (the heating and cooling rates of the temperature were chosen to be $5^\circ\text{C}/\text{min.}$ and $3^\circ\text{C}/\text{min.}$, respectively). Second group sample heated and cooled quench (SC). Third group sample heated and cooled rapid quench (FC) (in liquid nitrogen). The temperature dependence of the resistivity of the samples was measured by the standard four probe technique. X-ray diffraction (XRD) analysis was carried out by a rigaku D/ Max-III C diffractometer using high intensity $\text{Cu K}\alpha$ radiation. The lattice parameters were determined from the d values of XRD peaks by a standard least-square.

Hardness measurements of the BSCOO samples were performed on polished surfaces with a digital microhardness tester at room temperature. A Vickers pyramidal indenter with different loads (0.245, 0.490, 0.980, 1.960, and 2.940 N) and a single loading time of 10s were applied and diagonals of indentation were measured with an accuracy of $\pm 0.1\mu\text{m}$. Indentations were made at different parts of the samples surface such that the distance between any two indentations was no less than two times the diagonal of the indentation mark to avoid surface effects due to neighbouring indentation. An average of 5 readings at different locations of specimen surfaces was taken to obtain reasonable mean values for each load.

3. Results and discussion

The T_c^{offset} of transition temperature values are 103 K, 101K and 91K for the FC, SC and NC samples, respectively. The transition temperature increases with increasing the cooling rate. This result is good agreement with previous result [6].

In order to investigate the effect of cooling rates on the mechanical properties, we measured the diagonal length as a function of test load. Conventional Vickers microhardness measurement consist of applying a load F on the material via geometrically defined indenter and after the indenter is

removed, measuring the characteristic dimension d of the resultant impression. The Vickers microhardness (apparent) values of different applied loads were calculated using the equation [12]

$$H_v = 1854 \cdot 4(F/d^2) \quad (\text{GPa}) \quad (1)$$

where F is the applied load in Newton (N) and d is the diagonal length of indentation mark in micrometer (μm). The calculated load dependent microhardness values for different applied loads are summarized in Table 1. Figure 1 shows the variation of microhardness as a function of applied load for the NC, SC and FC samples. The variation of microhardness with load has similar shape irrespective of the cooling rates, although the numerical values are different. We have observed that the microhardness values increased with rapid quench cooling (FC). The reason for this ascribed to rapid quench cooling filling the intergrain space, resulting in better grain growth and causing larger grains, as a result leading to remarkable increase in the mechanical resistance of the samples. It was observed that Vickers hardness increased with increasing amount of doping in Bi-2223 superconductors [13-16]. It is also obvious from the figure that the Vickers microhardness values are load dependent for all samples; the calculated microhardness value decreases non linearly as the applied load decreased until 2N, then it tends to attain saturation. As reported by Khalil [14], this behaviour can be explained as follows; (a) at larger indentation loads, the Vickers hardness registered smaller values, this observation may be due to the presence of weak grain boundaries of the superconducting ceramics; (b) at smaller indentation loads, the Vickers hardness recorded higher values, this is ascribed to the fact that the measured hardness values were more indicative of the monocrystalline state without interference from grain boundaries. This non-linear behaviour has also been observed in the literature for Bi-Pb-Sr-Ca-Cu-O samples [13,14,17] and is known as the indentation size effect (ISE) [18-21].

Table 1. The load dependent values of H_v , E , Y , K_{IC} and B_i for the samples.						
Sample	F (N)	H_v (GPa)	E (GPa)	Y (GPa)	K_{IC} (Pa.m ^{-1/2})	B_i (m ^{1/2})10 ⁺⁵
NC	0.2450	0.4573	37.4819	0.1524	492.1	9.2920
	0.4900	0.4282	35.0973	0.1427	476.2	8.9915
	0.9800	0.3785	31.0219	0.1262	447.7	8.4534
	1.9600	0.3511	28.7735	0.1170	431.2	8.1413
	2.9400	0.3313	27.1520	0.1104	418.9	7.9085
SC	0.2450	0.4789	39.2523	0.1596	510.1	9.3876
	0.4900	0.4481	36.7278	0.1494	493.5	9.0807
	0.9800	0.3757	30.7937	0.1252	451.8	8.3148
	1.9600	0.3557	29.1544	0.1186	439.7	8.0905
	2.9400	0.3423	28.0561	0.1141	431.3	7.9366
FC	0.2450	0.5100	41.8014	0.1700	551.6	9.2450
	0.4900	0.4736	38.8215	0.1579	531.6	8.9094
	0.9800	0.3824	31.3407	0.1275	477.7	8.0051
	1.9600	0.3588	29.4047	0.1196	462.7	7.7539
	2.9400	0.3536	28.9802	0.1179	459.3	7.6978

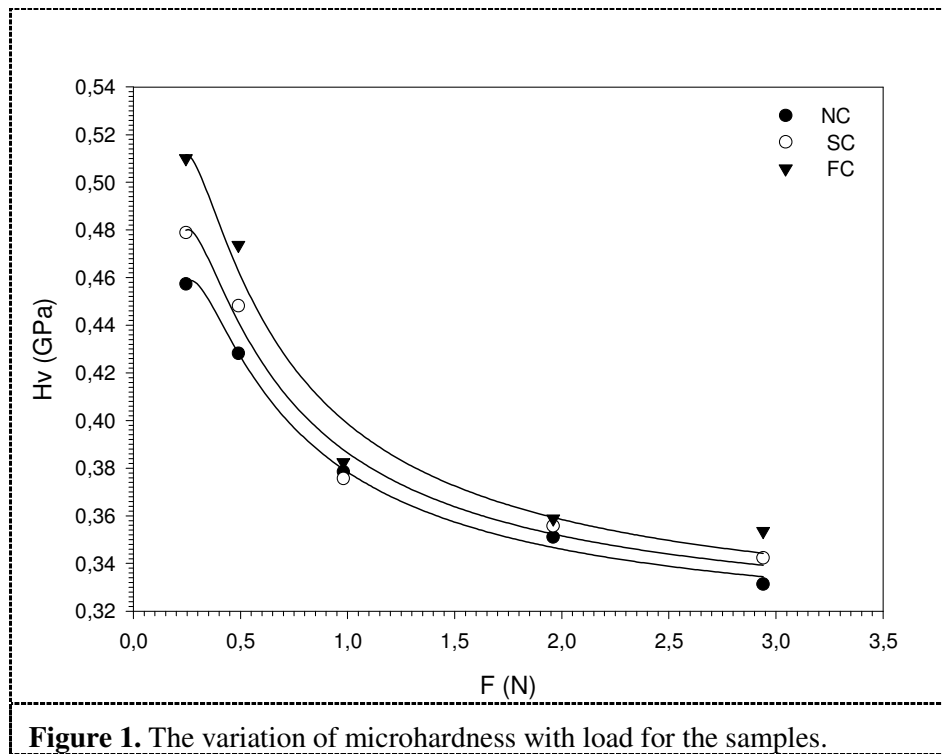


Figure 1. The variation of microhardness with load for the samples.

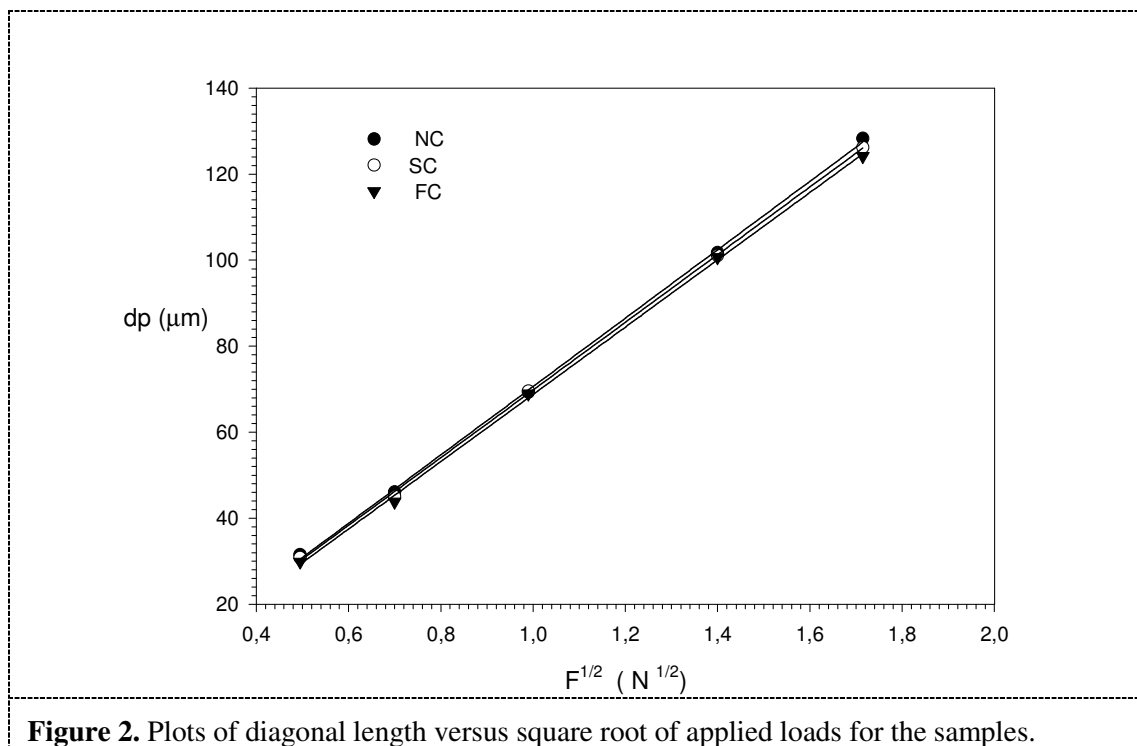
To account for this effect, several relationships between the applied load and the resulting indentation size have been suggested [22–25]. This effect can be explained by two different methods [12]. The first method assumes that the indentation contains an elastic portion. The elastic part of the deformation is relaxed upon loading. This can be accounted for by adding an elastic component, d_e , to the measured plastic indentation semidiagonal, d_p . Thus, a true hardness, H_0 , is defined from [12, 26]

$$H_0 = 1854,4 \left(\frac{F}{(d_p + d_e)^2} \right) \quad (\text{GPa}) \quad (2)$$

Therefore, Eq. (2) indicates that measured indentation diagonals should be linear with the square root of the applied load and the slope of such a curve is proportional to $(H_0)^{-1/2}$ and the vertical intercept of this graph is proportional to the elastic part of the indentation semi diagonal, d_e . The load dependence of the indentation diagonals for the NC, SC and FC samples was reanalyzed as d_p versus $F^{1/2}$ plots, as in Fig. 2. It was obvious that such plots are linear with the estimated linear regression coefficients (LRC) always better than 99.9%, implying that Eq. (2) provides a satisfactory description to calculate the true hardness of the indentation data for the samples. The extracted values of H_0 , d_e and LRC are listed in Table 2. As can be seen from the table, it was observed that the values of H_0 of the samples decreased slightly but that of d_e increased. Quin et al. [27] investigated the variation of Vickers microhardness as a function of indentation load for a variety of ceramic materials. They observed that such a hardness–load curve shows a distinct transition to a plateau of the constant hardness level and concluded that the transition in such curves corresponds to the intrinsic hardness value of the material. In this study, this plateau is reached at 2 N applied load for the samples. As can be seen from Table 2, the true microhardness value of the NC sample (0.795 GPa) is higher than the hardness results (see Table 1) in the plateau (saturated) region ($H_v = 0.331$ and 0.351 GPa). This behaviour is observed in other samples (SC and FC) in this work. This result indicates that the true hardness of the sample is higher than that of the traditionally calculated ones. The calculation of the H_0 values for the investigated samples also indicated the magnitude of d_e to be 8.8 for NC and 8.9–9.4 μm for SC and

FC samples. These extracted magnitudes of d_e infer that the amount of relaxation of the diagonal length is significant with respect to the measured diagonals at low indentation loads [28] and hence the ISE is pronounced for the low load range. This method has been applied to YBaCuO and BiPbSrCaCuO [12,26,28] materials but consistency was not very good.

Table 2. Best-fit results of experimental data corresponding to Eq. (2).				
Samples	H_0(GPa)	d_e(μm)	LRC	H_v (GPa) in plateau region
NC	0.783	8.875	0.99952	0.331–0.351
SC	0.787	8.911	0.99963	0.342–0.356
FC	0.795	9.451	0.99933	0.354–0.359



The second method considers energy dissipative processes during the indentation rather than elastic processes. In this model, a true microhardness can be defined by subtracting a dissipative part, F_0 , from the applied load [12]

$$H_0 = 1854,4 \left(\frac{F - F_0}{d^2} \right) \quad (\text{GPa}) \quad (3)$$

Fig. 3 shows applied load as a function of the square of the diagonal length for the samples. Each set of data shows an excellent linear relationship ($LRC > 0.999$). The slope of each line corresponds to the load independent hardness constant, H_0 , and the intercept of each line represents the sample resistance pressure, F_0 . The extracted values of F_0 , H_0 and LRC are listed in Table 3. As can be seen from this table, the values F_0 of the samples decreased and the values H_0 of the samples increased with decreasing the cooling rates. The LRC of each sample is very high, implying that Eq. (3) provides a satisfactory description of the indentation data for the samples. The energy dissipation model is also

supported in our work by Fig. 4, which shows a typical impression of the NC sample for a load of 0.98 N.

Table 3. Best-fit results of experimental data corresponding to Eq. (3).			
Samples	H₀(GPa)	F₀(N)	LRC
NC	0.174	0.117	0.99939
SC	0.179	0.108	0.99953
FC	0.184	0.107	0.99967

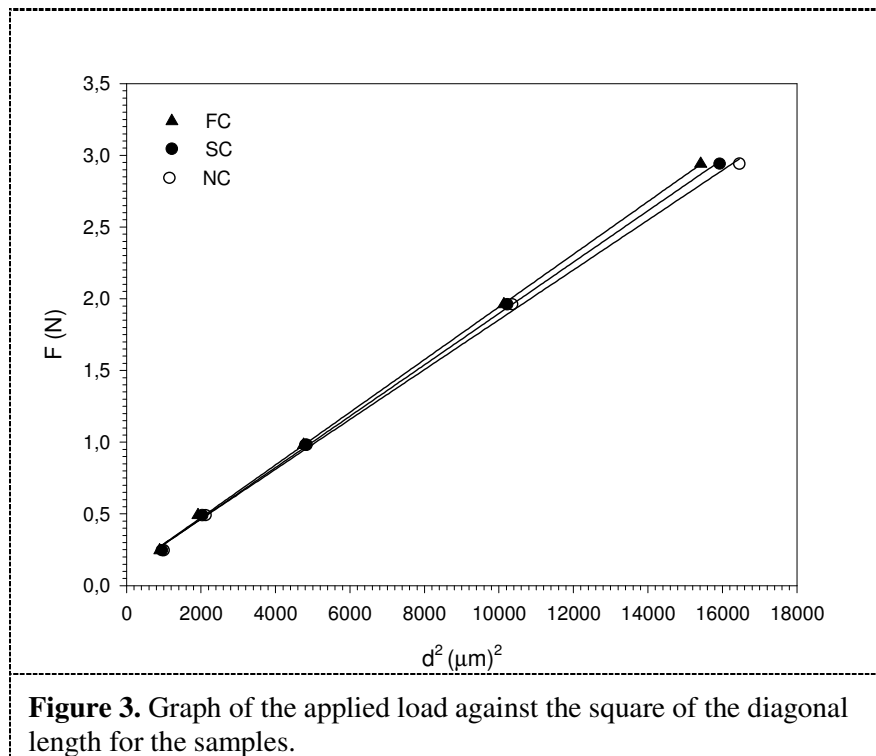


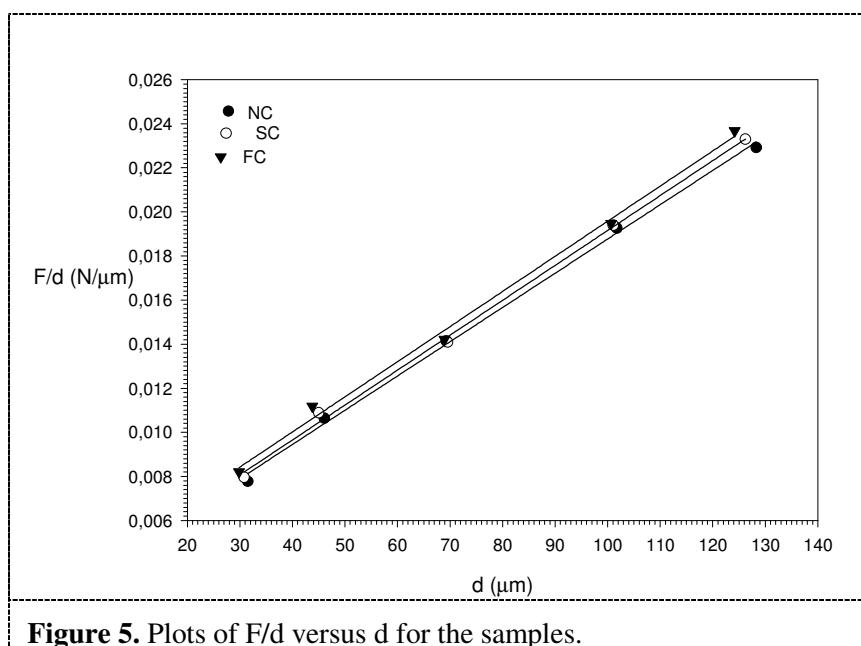
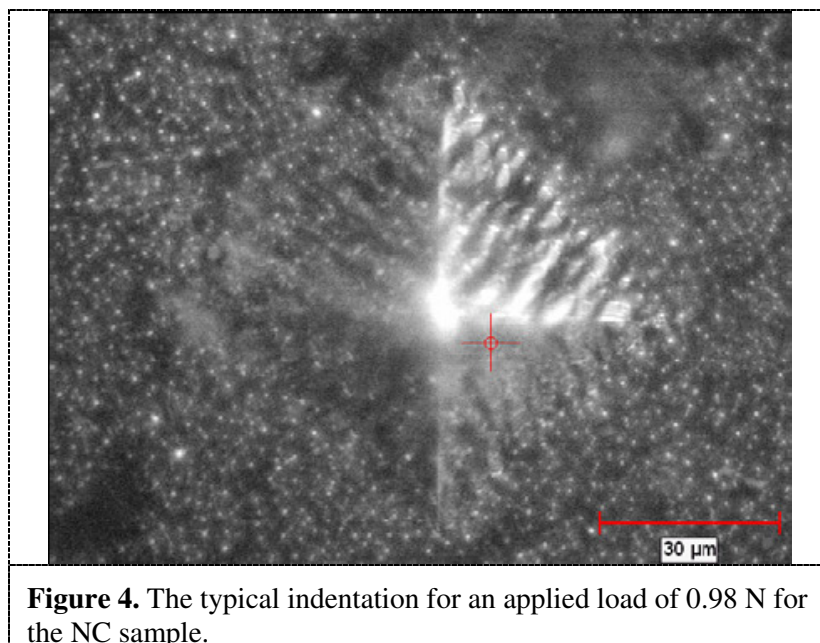
Figure 3. Graph of the applied load against the square of the diagonal length for the samples.

On the other hand, it is observed that the diagonal length is strongly dependent on the applied load from the experimental observations. This observation is governed by

$$\frac{F}{d} = H_0 d + \gamma \quad (4)$$

proposed in [13,22,29,30]. Fig. 5 shows the values of F/d against the diagonal length of indentation, d , for the samples. Each set of data shows an excellent linear relationship. The slope of each line corresponds to the true hardness, H_0 , and the intercept of each line represents the surface energy, γ . The extracted values of H_0 , γ and LRC are listed in Table 4. It is observed that the values of H_0 and γ of all samples increased with decreasing cooling rates. This observation is ascribed to the dissipation of the energy of cracks at the interfaces [12] and a similar behaviour in ceramics was also reported in indentation studies [13,30,31].

Table 4. Best-fit results of experimental data corresponding to Eq. (4).			
Samples	$H_0(\text{GPa})$	$\gamma \times 10^{-3} (\text{N}\mu\text{m}^{-1})$	LRC
NC	1.554	3.231	0.99976
SC	1.584	3.315	0.99980
FC	1.594	3.640	0.99960



In most materials, the elastic modulus (Young's modulus), E , is related to the Vickers microhardness (apparent) by the relation [11]

$$E = 81.9635H_v \quad (5)$$

and yield strength Y is related to the hardness by the relation [32, 33]

$$Y \approx H_v/3 \quad (6)$$

The values of load dependent E and Y were calculated for each load using Eqs. (5) and (6), and are summarized in Table 5. As seen in this table, the load dependent E and Y decrease significantly with increasing cooling rates and loads. This behaviour is due to crack initiation and improvement of microhardness. Similar changes in the yield strength and elastic modulus were reported in the literature [11,34].

Table 5. The load independent values of H_v , E , Y , K_{IC} and B_i for the samples.					
Samples	H_0 (GPa)	E (GPa)	Y (GPa)	K_{IC} (Pam^{-1/2})	B_i(m^{1/2})
NC	0.1540	12.6224	0.4620	285.6	53.92
SC	0.1580	12.9502	0.4740	293.0	53.93
FC	0.1590	13.0322	0.4770	308.0	51.62

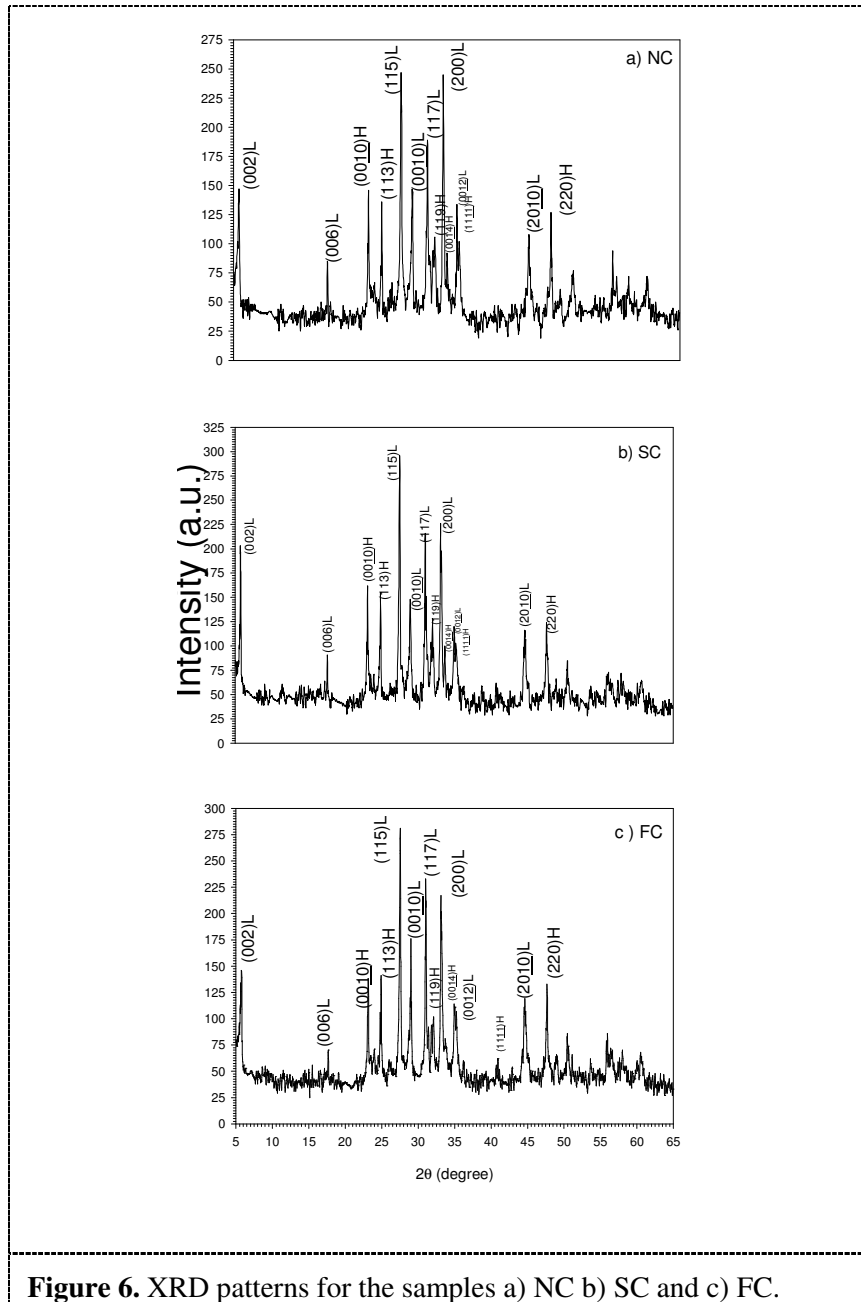
It is useful to mention the fracture toughness, K_{IC} , as it is one of the main mechanical properties of superconducting samples. The fracture toughness is an important parameter for the selection of materials for applications. Owing to the nature of intrinsic brittleness, microindentation may result in microfracture around the impressed region on the surface of the samples [35]. As microfracture occurs mainly during the loading a portion of the energy, which is used to create the indentation deformation, will be dissipated by the crack formation. Owing to the definition of K_{IC} as the critical stress intensity factor, it is directly related to γ of the crack faces [36, 37]

$$K_{IC} = \sqrt{2E\gamma} \quad (7)$$

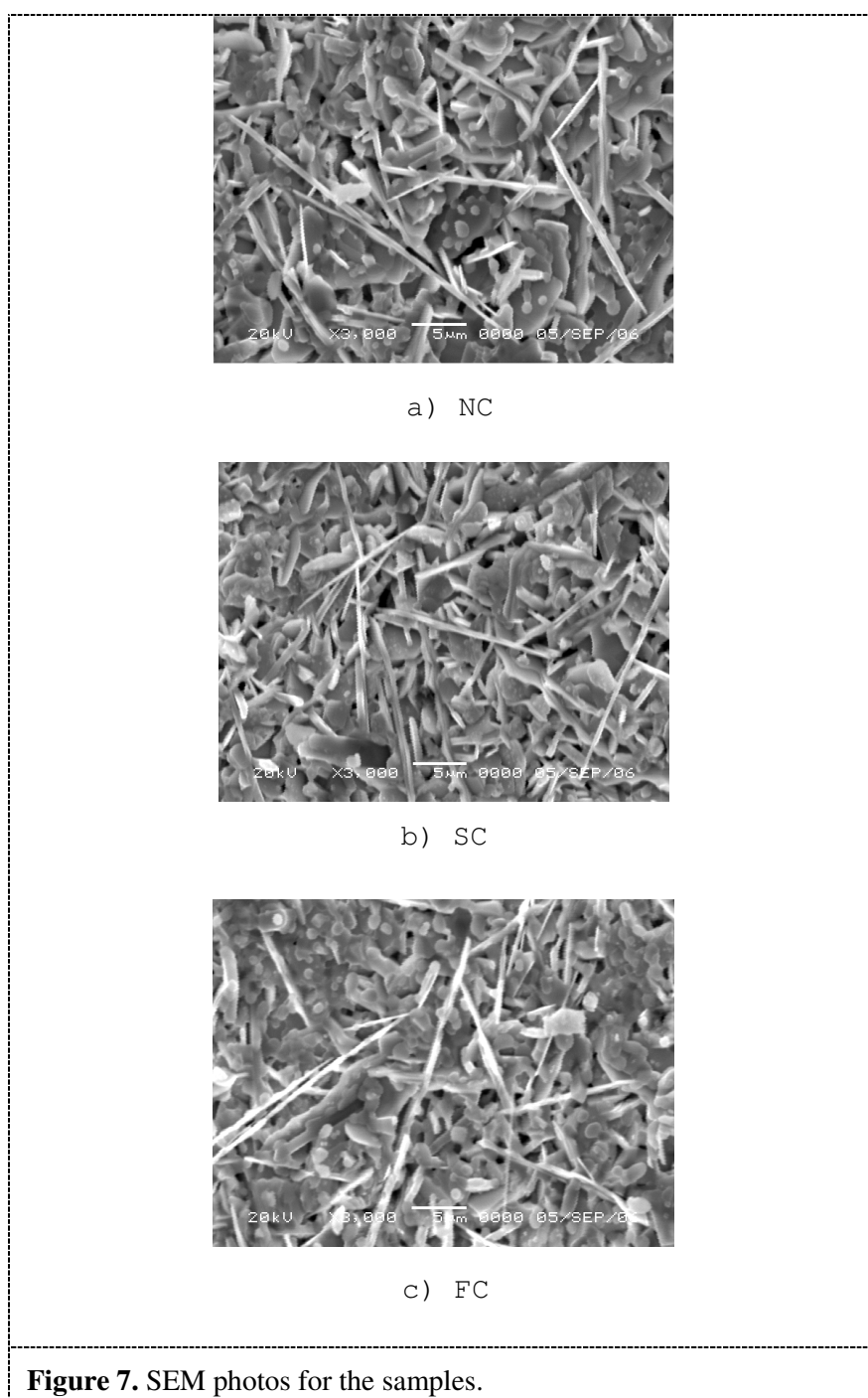
where E is the load dependent Young's modulus. The values of load dependent K_{IC} were calculated using Eq. (7) and are summarized in Table 1. From this table, it is observed that K_{IC} increases significantly with increasing loads. A similar change in the fracture toughness was reported in the literature [31,34]. Owing to this relation, an increase in K_{IC} corresponds to an increase in the average surface energy as proposed from the hardness calculations. From the values of K_{IC} and microhardness, one can calculate the brittleness index, B_i , using the relation [38]

$$B_i = \frac{H_v}{K_{IC}} \quad (8)$$

The calculated values of load dependent B_i for each load is listed in Table 1. From the table, it was observed that the brittleness index is load dependent up to 2 N and then remains close to a saturation value at higher applied loads for all samples. Note that the apparent microhardness, Young's modulus, yield strength, fracture toughness and brittleness index of the samples in the present work indicate strong dependency on applied load. In addition, we focused on the load independent values of Young's modulus, yield strength, fracture toughness and brittleness index of the samples. Instead of using apparent microhardness (H_v) values to calculate load dependent Y , E , K_{IC} and B_i in Eqs. (5)–(8) for each load, one can calculate E , Y , K_{IC} and B_i using true microhardness (load independent, H_0)



calculated by Eq. (4) for each sample. The obtained load independent Y , E , K_{IC} and B_i for the samples are tabulated in Table 5. From the table, it is observed that the load independent values of E , Y , K_{IC} increase, whereas that of B_i decrease. Comparing Tables 1 and 5, one can conclude that the load independent values are lower than those of the load dependent values. This is in agreement with the literature [12,39]. The above results revealed that by influence of cooling rates, it is possible to control the mechanical properties of the samples.



The XRD patterns from surface of the samples are shown in Fig. 6. Miller indices are indicated in the figure. (hkl)H and (hkl)L mean high-T_c phase (Bi-2223) and low-T_c phase (Bi-2212), respectively. We used the linear least squares method to calculate the lattice parameters of the samples. All of the samples are almost low phases. Comparison of XRD patterns did not reveal any significant shift at position of the peaks.

The structure of surface morphology of the samples was studied by SEM in order to determine the grain sizes. Fig. 7 shows surface micrographs for the NC, SC and FC samples. Grain size was small and granularity was apparent with sub-micron grains. Together with the XRD results, we deduce that the annealing temperature was lower than optimum and as a result grain connectivity was not sufficient.

4. Conclusion

This research represents the experimental results of cooling rate effect on Bi_{1.6}Pb_{0.4}Sr₂Ca₂Cu₃O_y superconductors prepared by standard solid state reaction methods. The phase evaluation, microstructure, and mechanical properties of the samples have been reported. XRD examination of the samples showed that the Bi-2212 phase increased while the Bi-2223 phase decreased with increasing the cooling rates. From SEM analysis, flake-like grains were more pronounced with increasing cooling rates. The indentation load versus diagonal length of the samples under different indentation loads in the range of 0.245-2.940 N were presented. We calculated Vickers hardness, Young's modulus, yield strength, fracture toughness values. These mechanical properties of the samples were found to be load and cooling rate dependent. Faster cooling rate degrades the denser microstructure of the surface morphology and mechanical properties. These degradations are due to an increase in voids, impurity phase and resistance to crack propagation and to a decrease in the contact area among the superconducting grains.

Acknowledgements

This work is supported partly by the Scientific and Technological Council of Turkey (Project No: 104T325) and partly the Turkish State Planning Organization (DPT) (Project No: 2004K120200).

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