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The effect of different dwell times at a constant pelletization pressure of 6 GPa on superconducting properties of $Bi_{1.8}Sr_2Ca_{1.1}Cu_{2.1}O_y$ ceramics

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Abstract In this study, the physical and magnetic properties of $Bi_{1.8}Sr_2Ca_{1.1}Cu_{2.1}O_y$ superconductors kept in different dwell times (1, 6, and 12 h) at a constant pelletization pressure of 6 GPa in the pressing step as prepared by standard solid-state reaction method are reported. The X-ray diffraction data shows that all samples have a tetragonal crystal structure with predominant Bi-2212. SEM micrographs for all samples predominately show plate-like grain structure, indicating the presence of Bi-2212 phase. Both T_c (onset) and T_c (offset) significantly increase with increasing dwell time. M–H measurements were performed at T = 10 and 25 K, respectively. In addition, J_c values of the samples were calculated from their magnetic hysteresis loops using the Bean's model. It has been found that J_c in the samples including long dwell times under the pelletization pressure of 6 GPa improves.

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1 Introduction

For the superconducting systems such as BSCCO and YBCO, the cation doping is generally done to improve the superconducting transition temperature (T_c) due to the increases in the density mobile holes in their CuO_2 planes [1–3]. However, the highest transition temperature (T_c) achieved in all high temperature superconducting families has a limited value according to the formation of the desired phases based on their chemical formulas. It is well known that BSCCO ceramics referred by the general formula $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ have three different phases which are called Bi-(2201), Bi-(2212), and Bi-(2223) according to their number of CuO_2 layers [4, 5]. The restricted transition temperature value for Bi-2223 phase including the highest transition temperature in BSCCO system is approximately 120 K by the appropriate amount of Pb doping while it is $T_c \approx 110$ K without any element substitution [6–8], showing the activity degree of cation doping on T_c. On the other hand, the critical current density (J_c) in the type II superconductors can significantly be increased by appropriate cation substitutions, which favor the formation of the desired phase [9–22]. When a high magnetic field is applied to a type II superconductor in the mixed state, the material can still be superconductor. However, electric fields occurred by the motion of vortex lines in this instance cause serious current carrying losses. It is well known that this problem can be solved by the formation of new effective pinning centers which can be created by appropriate cation doping, ensuring high J_c.

On the other hand, J_c values are generally based on internal morphological parameters such as the orientation and size of grains, vacancies, defects, and the presence of impurities within a crystal structure. The methods used for the preparation of ceramic superconductors also strongly

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influence these morphological properties. Thus, many studies on the innovation of sample preparation techniques as well as the searching of useful cation substitution/doping into high temperature superconductors have been made to support the desired phase formation or more regular grain orientation in superconducting systems [9, 23–25].

In the previous study, we synthesized polycrystalline Bi-2212 samples with extremely high pelletization pressure values by using the solid state reaction method [26]. The best superconducting properties of Bi-2212 phase in that work have been obtained by cold isostatic pressing with an applied pressure of 6 GPa, indicating that one of the important factors affecting J_c is the pelletization pressure values applied during sample preparation. In the preparation of many high-T_c superconductors, it is well known that the conventional solid-state reaction method is commonly used because of its relatively simple and economical processes such as grinding, mixing, and annealing. In addition, pressing as well as calcinations and annealing processes used in that method is a highly important preparation step, ensuring more homogeneous and denser materials without the porosity due to the easier aggregate of atoms, ions or molecules for the formation of desired phases.

In this study, we have compared the superconducting properties of Bi-2212 phase prepared under different dwell times (1, 6, and 12 h) while pelletization pressure is kept constant at 6 GPa. Superconducting properties of prepared samples were investigated by XRD, SEM, R–T, and M–H loops.

2 Experimental details

High purity powders of commercial Bi_2O_3 (Panreac, 98+ %), $SrCO_3$ (Panreac, 98+ %), $CaCO_3$ (Panreac, 98.5+ %), CuO (Panreac, 97+ %) were used for the preparation of samples in this study. Polycristalline samples with nominal composition $Bi_{1.8}Sr_2Ca_{1.1}Cu_{2.1}O_y$ were prepared by the standard solid-state reaction methods. Firstly, they were weighed in the appropriate proportions. Precursor powders were then mixed by milling for 2 h in the air in an agate mortar to get a homogeneous mixture.

After the milling process, the homogenous mixture of powders was pressed into pellets of 2.9 cm diameter by three different dwell times including 1, 6, and 12 h at the constant pelletization pressure of 6 GPa at room temperature and then calcined at 750 °C for 12 h. The pellets calcined in the high temperature furnace were thoroughly reground. Then, they were repressed within their different dwell times at pelletization pressure of 6 GPa applied as uniaxial at room temperature and recalcined at 820 °C for 24 h to start the formation of the superconducting phase. It is obvious from the literature that it is possible to reach larger *M–H* curves in BSCCO system when the pelletizing process is repeated [26, 27]. Thus, these processes based on the milling, sintering, and pressing were repeated two times. Finally, ceramic materials including different dwell times at pelletization pressure of 6 GPa were annealed at 850 °C for 120 h in the air to produce the Bi-2212.

Taking into account the dwell times at a constant pelletization pressure of 6 GPa, the samples will be herein after denoted as A, B, and C, respectively.

Resistivity and magnetic measurements were carried out on samples using Cryogenic Limited PPMS (from 5 to 300 K) which can reach the cryogenic temperatures about to 2 K in a closed-loop He system. X-ray powder diffraction analyses to determine the phases present in the samples were performed by using a Rigaku Ultima IV X-ray diffractometer with a constant scan rate (2°/min) in the range $2\theta = 3°–60°$. The surface morphologies of the samples were studied by using a Zeiss/Supra 55 Scanning Electron Microscopy (SEM).

The pressing of samples was made by using Special Press with model version 22170, which can reach the maximum pressures about to 15 GPa pressing force with 1300 * 1600 mm table sizes designed by Hursan Hydraulic Press and Workbech Ind.Set.CO, ODCP Series.

In addition, hardened to 48HRC steel mold was used in order to press the samples at targeted pressing forces.

3 Results and discussion

3.1 XRD studies

Figure 1 shows the powder X-ray diffraction patterns for all samples. There are Bi-2212 and Bi_2CaO_4 phases in all samples (shown in Fig. 1 by + and *, respectively). However, some peaks of Bi_2CaO_4 impurity phase appeared in both A and C samples such as $2\theta \approx 31.7°; 36.2°; 56.7°$ disappear in sample B. Thus, higher T_c values in sample B can be expected by decreasing the amount of these impurity phases causing weak links between grains in polycrystalline superconductors.

It has also been found that the peak intensities of Bi-2212 phase in all the samples are significantly high, implying well crystallinity of samples. It is clear that the variation of the peak width in XRD graphics depends on crystal morphologies such as crystal size and crystal shape while high intensity in peak positions is related to the texturing degree of grains [28–30]. The high intensity of Bi-2212 phases and their peak positions in all samples do not change significantly, showing that a significant phase transformation does not occur in samples.

On the other hand, lattice parameters determined automatically from the XRD diffraction data are listed in

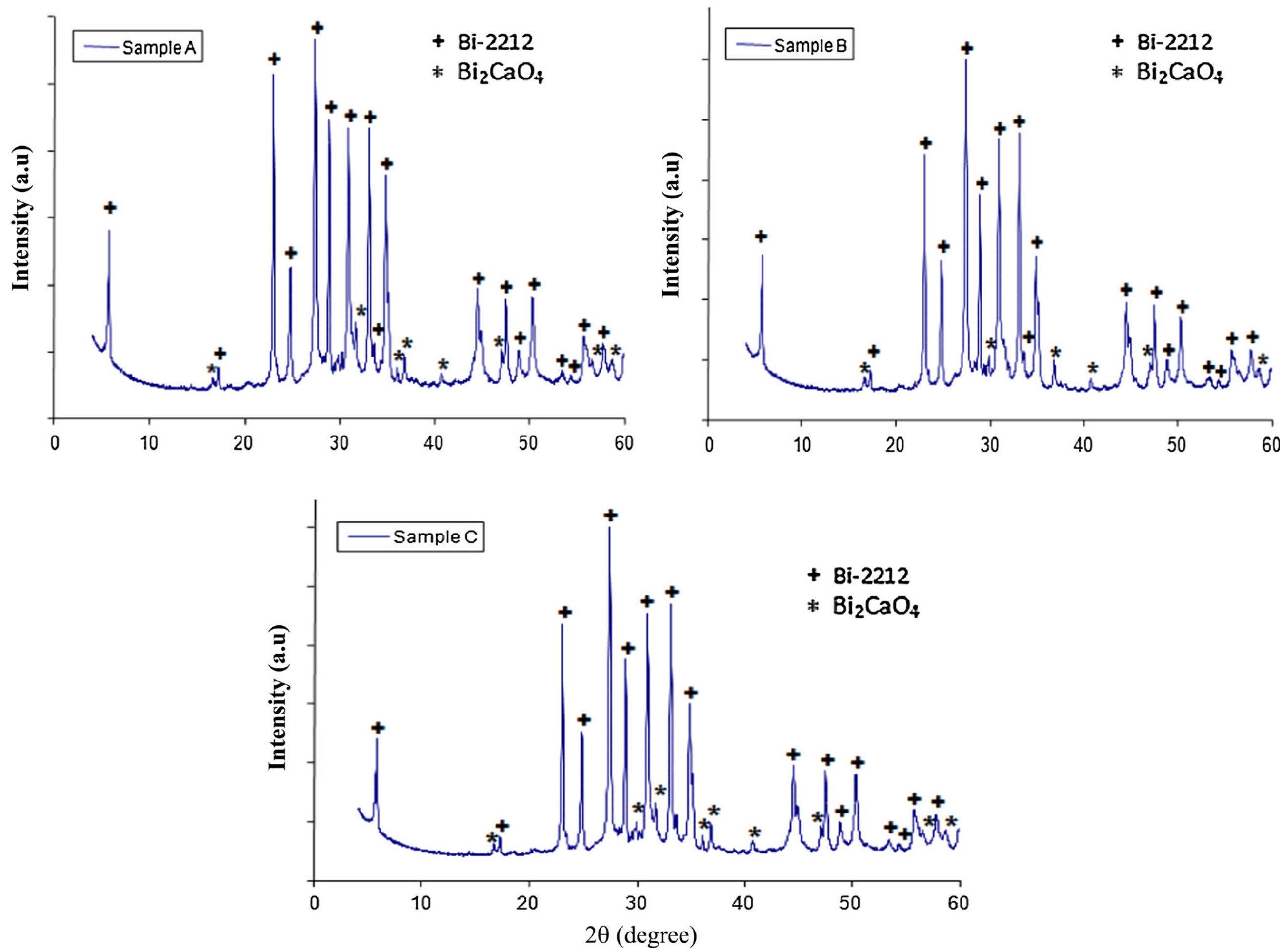

Fig. 1 XRD patterns of the **A**–**C** samples. The peaks of Bi-2212 and Bi_2CaO_4 are shown by *plus* and *asterisk*, respectively

Table 1 Crystal parameters and resistivity measurement results for the samples

Samples	a (Å)	b (Å)	c (Å)	T_c^{onset} (K)	T_c^{offset} (K)	R (mohm-cm) at 150 K
A	5.4046	5.4046	30.836	78.4	57.8	2.12
B	5.4093	5.4093	30.809	94.8	75.4	1.95
C	5.4173	5.4173	30.881	93.7	67.6	1.7

Table 1. All samples have a tetragonal crystal symmetry. The c-axis showing length in the Bi–O double layers in BSCCO ceramics is in the region of 30.809–30.881, which is an another evidence showing the stable structure of the Bi-2212 phase and the formation of similar phase in all samples.

3.2 SEM analyses

SEM micrographs for all samples are shown in Fig. 2a–c. The crystalline phases with randomly oriented plate-like grain were observed in all samples, showing the predominance of Bi-2212 phase. Sample C including the dwell time of 12 h at the constant pressure of 6 GPa had bigger grain size than other samples, indicating that the high dwell time as the pelletization pressure of 6 GPa can ensure further rapprochement of atoms and molecules in the process of nucleation to better support the composition of Bi-2212 phase. However, the growth of big plate-like grains observed in sample C is random in the c-axis direction, creating big holes between grains, which negatively affects inter-grain connectivity. On the other hand, sample B has more granular surface, implying better grain couplings and stronger grain boundaries even if its grain size is smaller than sample C.

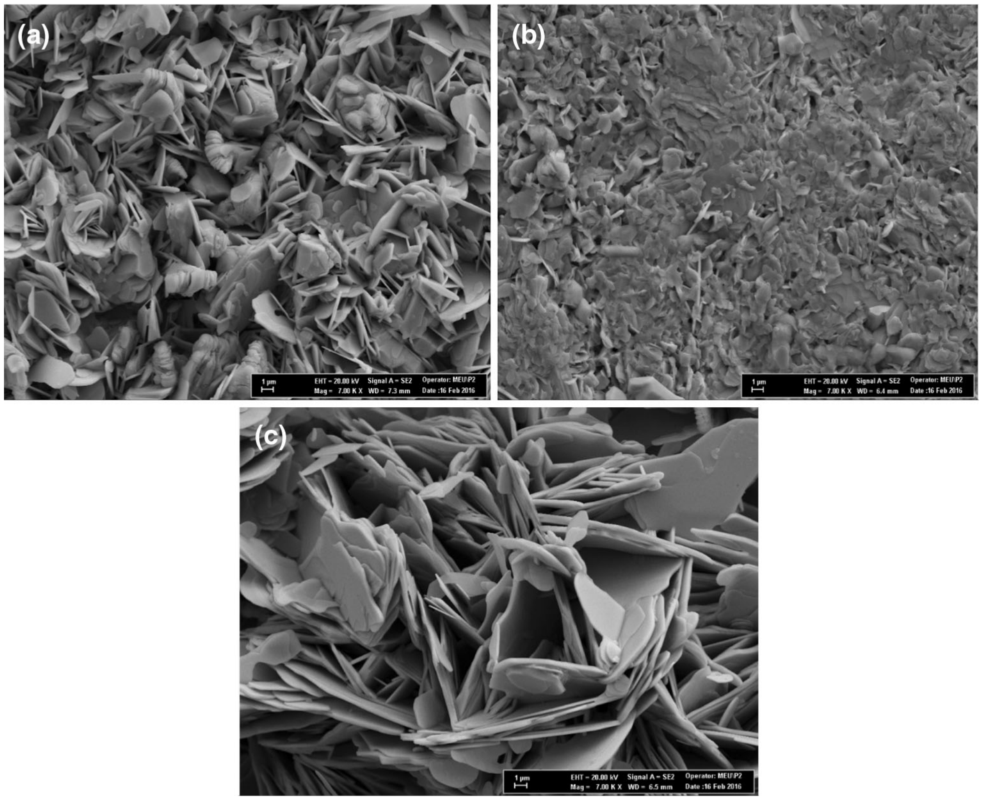

Fig. 2 SEM micrographs obtained in the surfaces of **a** A; **b** B; and **c** C samples

3.3 Electrical measurements

Figure 3 shows the electrical resistivity versus temperature curves for all the samples, from 5 to 150 K. The T_c (onset) values for the A, B, and C samples have been found to be about 78.4, 94.8, and 93.7 K, respectively (see Table 1).

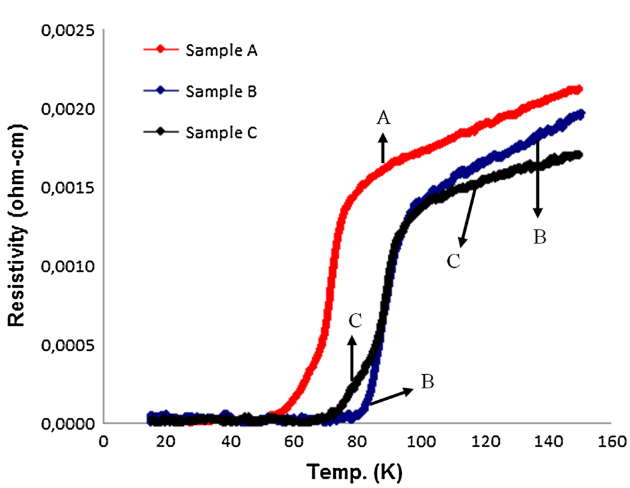

Fig. 3 Electrical resistivity as a function of temperature curves for all the samples

Despite the fact that all samples have one-step superconducting transition from the normal state to the beginning of the superconducting state (T_c^{onset}), which implies metallic behavior, they have different transition temperatures due to different coherence between their grains. The small broadening in the superconducting transition for sample B can be explained by the formation of strongly coupled grains.

By comparing the dwell period, it was found that the highest T_c (offset) value was obtained for sample B. The results clearly show that dwell process as well as the applied high pelletization pressure values significantly affects the nucleation and growth behavior even if it does not create important effects on the formation of impurity phases affected the crystallization kinetics.

3.4 Magnetic properties

The magnetic-hysteresis cycles, between applied fields of ± 2 T, for all the samples at 10 and 25 K, are presented in Figs. 4 and 5, respectively.

It is obvious that sample B has the largest M–H loop at both 10 and 25 K as compared to other samples. It is well known that the high temperature superconductors such as BSCCO and YBCO can easily prevent the vortex motion

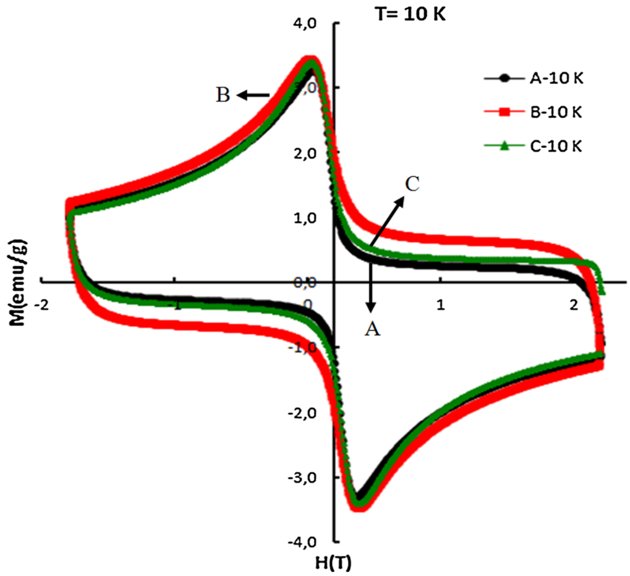

Fig. 4 Magnetization hysteresis curves for all samples measured at 10 K and ±2 T external applied magnetic field

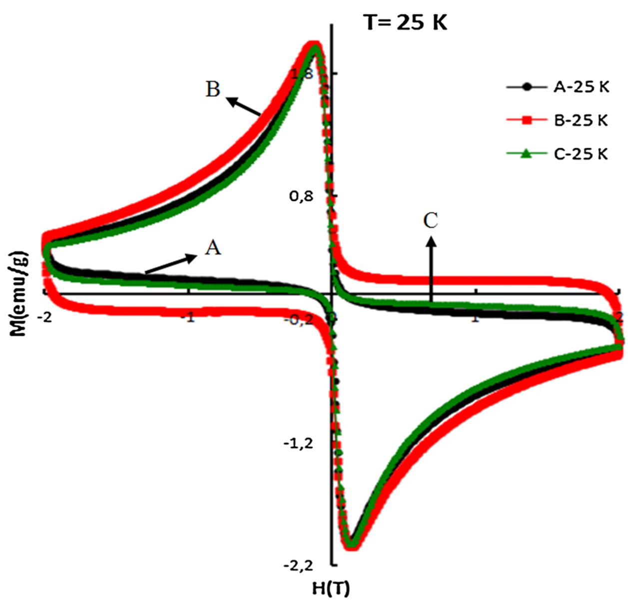

Fig. 5 Magnetization hysteresis curves for all samples measured at 25 K and ±2 T external applied magnetic field

when the applied temperatures and magnetic fields are low. However, with the increase of these parameters J_c values can decrease rapidly. Thus, some parameters such as the presence of effective pinning centers or the formation of well connected grains for superconductors are vital in achieving the high J_c values at high temperature and magnetic fields. One of the characteristics of type II superconductors is the existence of the large ΔM in the their M–H loops when they especially have granular and

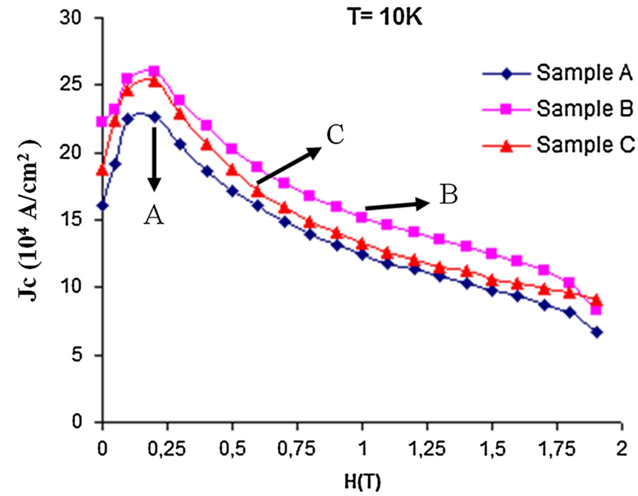

Fig. 6 Calculated critical current densities for all the samples at 10 K as a function of applied field

homogeneous microstructure containing the desired superconducting phases without secondary phases destroyed connectivity between grains.

The shape of the hysteresis curves due to diamagnetic response to the applied *H* fields for all samples even at 25 K is almost the same, indicating the presence of similar phases in samples as clearly seen from our XRD results. However, the magnitude of the hysteresis loops in samples significantly changes, showing the effects of dwell times on the size and orientation of grains.

The J_C values of the samples were calculated at T = 10 K, using the Bean's model [31]:

$$J_C = 30\frac{\Delta M}{d}$$

where J_C is the magnetization current density in ampéres per square centimeter of a sample. $\Delta M = M_+ - M_-$ is measured in electromagnetic units per cubic centimeter, d is the diameter of cylindrical samples.

Figure 6 shows the effect of dwell times at a constant pelletization pressure of applied 6 GPa on intergrain critical current density (J_c) of the Bi-2212 ceramics. It is obvious that J_c curves obtained by the *M–H* loops of samples are compatible with the width ΔM of the M(H) hysteresis loop of samples, as expected. Enhancements in J_c values for sample B reflect better intra and inter grain coupling as depending on the dwell time of 6 h. These results clearly show that the superconducting properties of BSCCO system optimized by pelletization pressure and its applied periods can be improved with the favorable variation of microstructures. The J_c value is highest (25.98×10^4 A/cm^2 at H = 0.2 T) for sample B through the applied magnetic fields.

4 Conclusions

In this study, the effect of different dwell times (1, 6, and 12 h) at a constant pelletization pressure of 6 GPa on the physical and magnetic properties of Bi-2212 phase has been investigated. X-ray diffraction patterns of the samples have shown that the amount of impurity Bi_2CaO_4 phase in sample B including the dwell time of 6 h decreases, suggesting the enhancements of Bi-2212 superconducting phase. The *M–H* hysteresis loops of the samples improve when high dwell times are applied. Also, the J_c values calculated from hysteresis loops of samples indicate that grain connectivity which plays crucial role in high-J_c values can be significantly increased by optimal dwell times at a constant pelletization pressure of 6 GPa.

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