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ORIGINAL PAPER

The Effects of Mg Substitution in Bi-2223 Superconductors

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Abstract The effects of Mg substitution in Bi-2223 superconductor system has been studied for the $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ nominal composition ($x = 0.00$, 0.05, 0.10, 0.15 and 0.20) which was prepared by the conventional solid-state reaction. The properties of these compounds have been investigated by measuring the electrical resistivity, X-ray diffraction (XRD) and density. Also, scanning electron microscopy (SEM) was employed to investigate the surface microstructure of the samples. It has been found that the effects of Mg substitution support the development of both the Bi-2212 and Bi-2223 phases. These measurements and analyses enable us to discuss the effects of Mg dopant on superconducting properties. We found that onset critical temperatures ($T_{c,\mathrm{onset}}$) decrease with addition $x > 0.10$ in resistivity measurements. The presence of Mg influenced the microstructure of the samples and decreased the mean grain size of Bi-2223 grains up to $x = 0.10$.

Keywords High-T_c superconductors · Mg substitution · Bi-2223 · X-ray diffraction (XRD)

1 Introduction

Since the discovery of BiSrCaCuO high-T_c superconductors [1, 2], great progress has been achieved in enhancing structural properties of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_y$ (Bi-2223) superconductor. Recently, many techniques have been developed to prepare superconductors. Doping is believed to be promising. It favors the 2223 phase formation and improves superconductivity. It is well known that the T_c value is significantly affected by preparation conditions, even if superconductors have the same compositions. Similarly the effect of doping on the 2223 phase formation and its superconductivity is also influenced by the preparation condition. Therefore, the T_c value alone could not define the relationship between the doping and the formation of high-T_c 2223 phase, especially as the 2201 and 2212 phase tend to coexist with the 2223 phase [3]. There have been many studies for Bi-2223 to improve its superconducting properties. Properties of BiSrCaCuO superconductors can be controlled by substituting elements that have different ionic radius and different binding characteristics. In the literature, effects of substituting specially alkali metal (Li, Na, K, Rb ve Cs) in Bi-based superconductors have been studied and it has been found that alkali metals decrease the temperature of the Bi-2212 phase very strongly. By the Li and Na addition, T_c has increased; however, it has decreased by the addition of K and Rb [4]. In our previous work [5], we investigated the effects of Li substitution on the properties of high-temperature superconductor $Bi_{1.7}Pb_{0.3}Sr_2C_2Cu_{3-x}Li_xO_y$. The X-ray diffraction results indicated that Bi-2223 phase is dominant with regard to Bi-2212 phase.

Kameli et al. [6] have investigated Mg substitution and the results have shown that the lattice parameter c decreases by increasing Mg doping. It seems that the decreased length of c-axis with increasing Mg content is due to the substitution of Ca by smaller ionic sized Mg in all samples. It can be seen from resistivity measurements that, while the superconducting transition temperature of the grains, T_c is almost

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the same for all the samples, the T_c ($\rho = 0$) is affected by post-annealing in oxygen.

Abbasi et al. [7] have investigated the $MgCO_3$ addition to Bi-2223 superconductors and Bi-2223 phase decreases while Bi-2212 phase increases with increasing dopant content. The lattice parameter c decreases with increasing $MgCO_3$ content, but the a parameter does not change considerably. It was also found that critical temperature and room temperature resistivity decreases with increasing dopant addition.

Guilmeau et al. [8] have studied MgO doping on the phase formation and microstructure of Bi-2223 compounds and they showed that formation of Bi-2223 is slowed down by the presence of MgO particles. It was also demonstrated that an increase of MgO content causes a decrease of the grain size by limiting the diffusion of elements during the sintering. In terms of physical properties, all the investigated superconductors, regardless the content of MgO, exhibit typical behavior of granular systems, i.e. a two-step transition. The high-temperature transition can be explained in terms of the superconducting transition of Bi-2223 phase, while the low-temperature one originates from the phase-locking of the grains or from the presence of Bi-2212 phase.

Lu et al. [9] have investigated the effect of MgO addition on (Bi,Pb)-2223 superconductors. The results have shown that Bi-2223 phase and Bi-2212 phase are the main constituents of the sample with different MgO doping amount. With increase of the MgO doping amount, the line intensities of Bi-2223 phase increase ($0 < x < 0.5$) and then decrease ($0.5 < x < 15$). A peak in the line intensities of Bi-2223 phase appears in the sample with $x = 0.5$. However, MgO addition did not affect the formation rate of Bi-2223 phase and could suppress the growth of Bi-free non-superconducting secondary phases [10].

In previous study, Kocabas et al. [11] showed that the optimal sintering temperature is about 845 °C, which is the highest density value and the highest volume fraction of Bi-2223 phase by the result of XRD. Moreover, the XRD results show that by increasing sintering temperature up to 845 °C, the Bi-2212 phase fraction decreases. SEM results indicate that the surface morphology of the sample is improved with increasing sintering temperature up to 845 °C.

In this study, we have investigated the effects of Mg ($r_{Mg} = 0.73$ Å) substitution in Cu ($r_{Cu} = 0.72$ Å) sites in Bi-2223 superconductors. We have discussed the results of electrical-resistivity measurements (R–T), X-ray powder diffraction analyses (XRD) and scanning electron microscopy (SEM).

2 Experimental Process

Mg substituted samples with nominal composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$, 0.05, 0.10, 0.15 and 0.20) were prepared by a solid-state reaction method using high-purity chemicals Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and MgO. Stoichiometric amounts of these oxide powders were weighed by Scaltec balance. After weighting, they were thoroughly mixed and ground using an agate mortar and pestle. We labeled our samples A ($x = 0.00$), B ($x = 0.05$), C ($x = 0.10$), D ($x = 0.15$), E ($x = 0.20$). They were calcined in air at 800 °C and 820 °C for 20 h with intermediate grinding. The calcined powders were ground again and uniaxially pressed into pellets of 13 mm diameter and 1.5–2 mm thick at 450–500 MPa compaction pressure. These pellets were sintered at 855 °C for 150 hours by using furnace and cooled down to room temperature in air. For all samples, resistance was measured as a function of temperature using the dc four-point probe technique. X-ray diffraction (XRD) patterns of Mg substituted samples were obtained by diffractometer in the $2\theta = 5°–60°$ range with CuK_α radiation. Scanning electron microscopy (SEM) images were taken by using a SEM microscope. The bulk densities were measured by the Archimed technique.

3 Results and Discussion

Variation of resistivity to temperature with Mg content for our samples is shown in Fig. 1. As to the slope of the resistivity-temperature curve, all samples showed metallic character above the onset critical temperature ($T_{c,\,\mathrm{onset}}$). Onset temperatures of A, B, C, D and E samples are 112 K, 108 K, 112 K, 110 K, and 104 K respectively. The resistivities corresponding to the onset temperatures of samples are 0.0025, 0.0043, 0.0033, 0.0062, and 0.0061 ohm cm respectively. It seems that onset temperatures decrease on addition $x > 0.10$ in our samples.

Critical temperatures ($T_{c,\,\mathrm{zero}}$) are found as follows in the samples; 67 K, 88 K, 94 K, 90 K, 78 K for A, B, C, D, E respectively. There is an increase of the critical temperature ($T_{c,\,\mathrm{zero}}$) with Mg addition and maximum increase is observed in the optimum sample, with $x = 0.10$.

Another physical property, specific for superconductivity, is ΔT_c, the transition temperature width, and it is defined by $\Delta T_c = T_{c,\,\mathrm{onset}} - T_{c,\,\mathrm{zero}}$. We expect that this broadening should be narrow in a good superconductor. The reduction in the broadening behavior may be due to the increase in the contact area among the superconducting grains [12]. Transition temperatures widths (ΔT_c) are calculated as follows for our samples respectively: 45 K, 20 K, 18 K, 20 K, 26 K. These values are shown in Table 1. By the substitution, there is a narrowing in the transition temperature width and the maximally narrow transition is seen on sample C. So we can say that sample C has a sharper transition curve than the others.

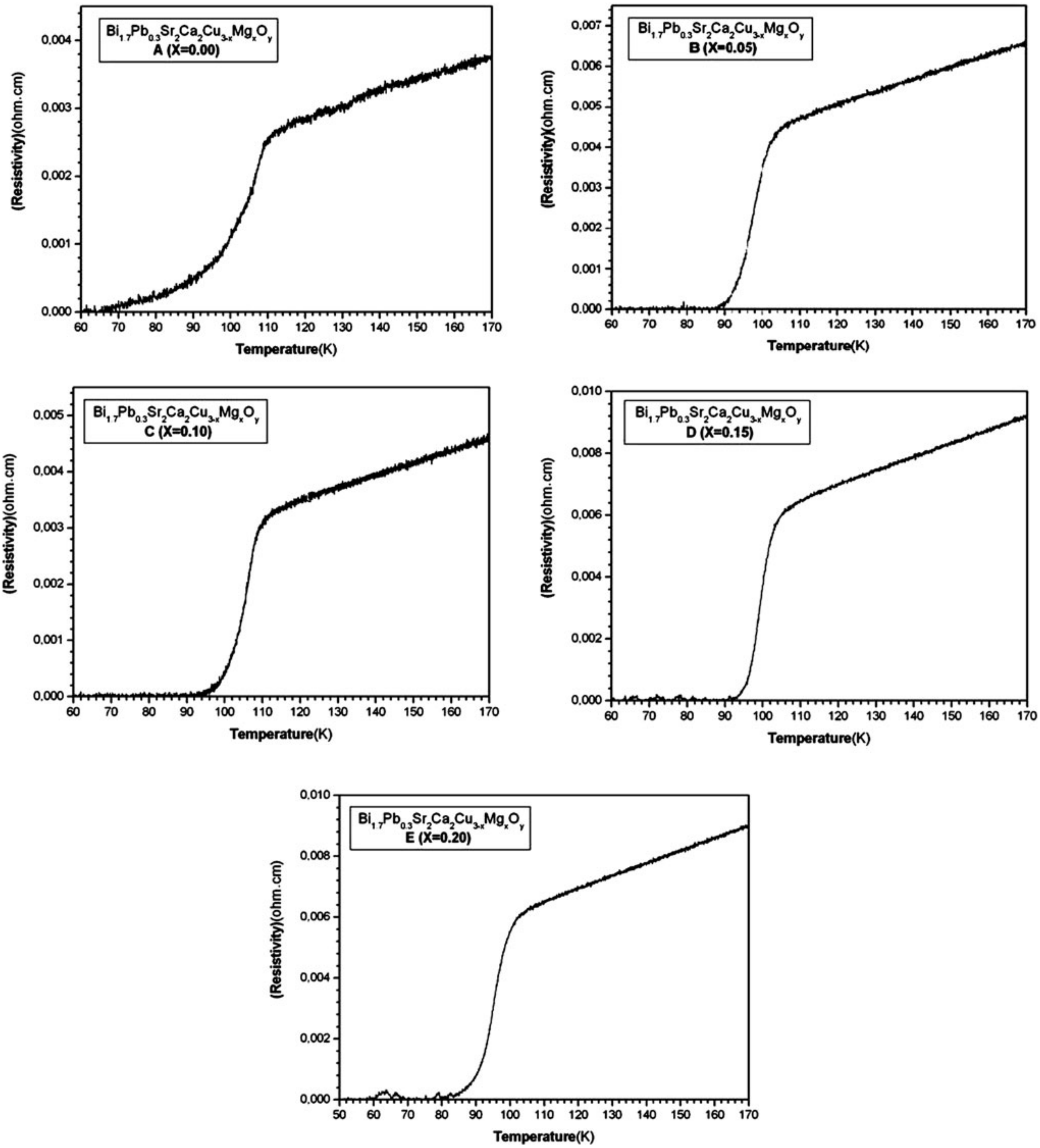

Fig. 1 Temperature dependences of the electrical resistivity for the samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$–0.20)

As we examine Fig. 2(c), ΔT_c has minimum value and maximum onset temperature in sample C. So we can say that optimum Mg concentration for T_c is seen in the $x = 0.10$ Mg doped sample. Also ΔT_c is maximum in the sample E, which has maximum Mg substitution with minimum onset temperature. So this may be evidence showing that the onset temperature and transition temperature are closely related. It can be said that an increase of the onset temperature can decrease ΔT_c.

The XRD patterns of the samples are shown in Fig. 3. It is seen that Bi-2223 high-T_c phase is dominant in our samples. Also we see that as Mg substitution increases, impurity

Table 1 $T_{c,\,\text{zero}}$ (K), $T_{c,\,\text{onset}}$ (K), ΔT_c (K) and density of the all samples

Sample	Mg (x)	$T_{c,\,\text{onset}}$ (K)	$T_{c,\,\text{zero}}$ (K)	ΔT_c (K)	Density (g/cm^3)
A	0.00	112	67	45	5.3326
B	0.05	108	88	20	5.1025
C	0.10	112	94	18	5.4177
D	0.15	110	90	20	4.9847
E	0.20	104	78	26	5.2841

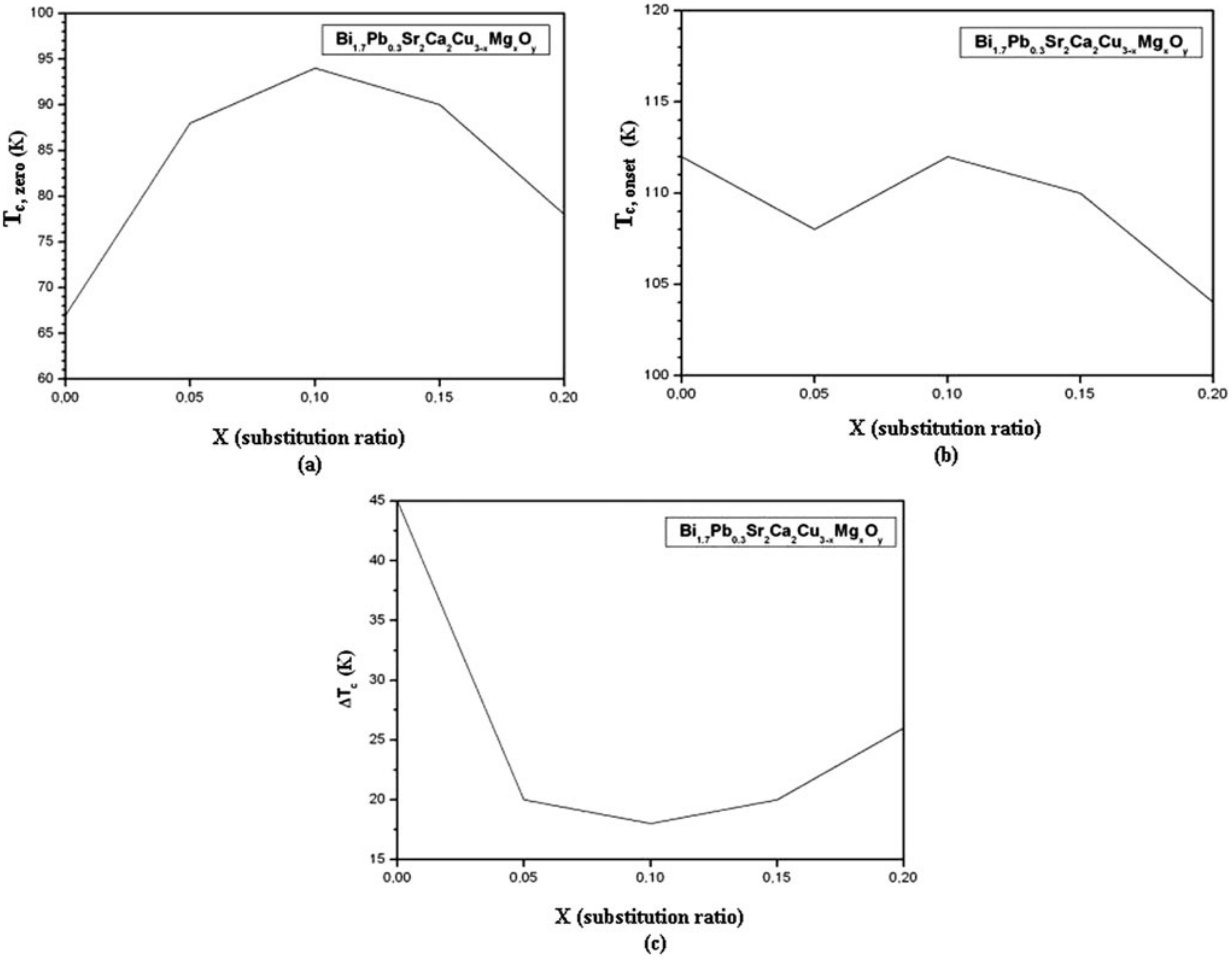

Fig. 2 Variation of (**a**) $T_{c,\,\text{zero}}$ (K), (**b**) $T_{c,\,\text{onset}}$ (K), (**c**) ΔT_c (K) with Mg content

phases and their intensities increases in the XRD patterns. L(002) peak which is the characteristic peak of Bi-2212 system, is observed at $2\theta = 5.7$ degree in all samples. Also the change of peak intensities to amount of doping is shown, in Fig. 4.

As we examine peaks between $2\theta = 23$–35 degrees, it is seen that the H(111) peak which corresponds to $2\theta = 23.28$ degree, has the highest intensity in sample E and its intensity has decreased in samples B and D. Also the H(0010) peak intensity, corresponding to $2\theta = 27.74$ degree, has reached a maximum value in the sample E; however, there is a decrease in its intensities for samples B and D. In both peaks, sample C increases intensity. In three peaks that we have examined till now there are same changes depending on the same substitution. So we can say that increasing the substitution ratio shows the same effect in these three peaks.

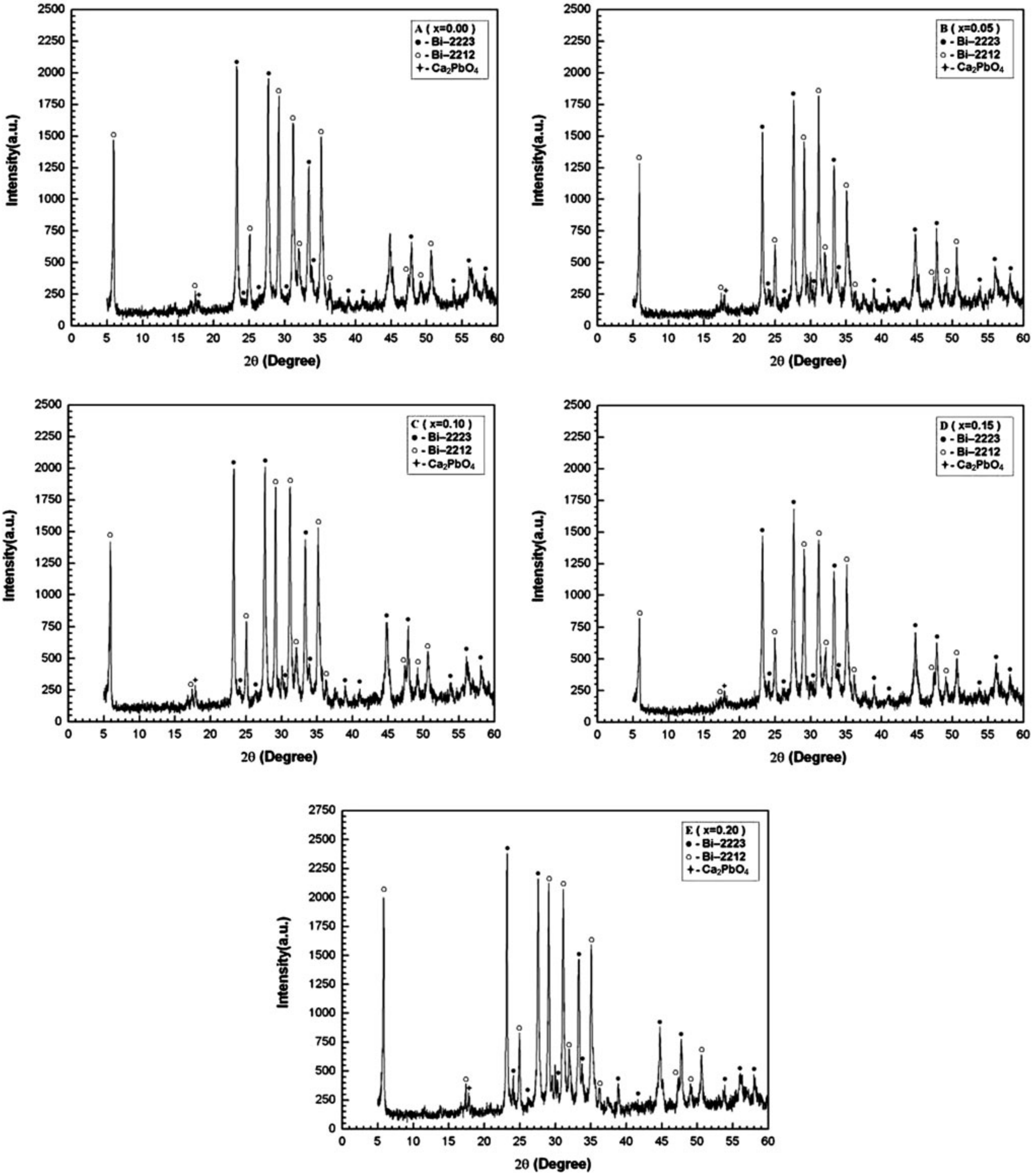

Fig. 3 XRD patterns of the samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$–0.20)

In $2\theta = 29.20$ degree the L(0010) peak intensity decreases in the samples B and D, however, it increases in samples E and C. It reached its maximum value in sample E, but in the $2\theta = 31.20$ degree L(117) peak there is an increase in intensity depending on Mg substitution.

In $2\theta = 33.44$ degree H(020) peak, there is no change in the intensity in samples A and B, whereas it increased in C and E and decreased in D. It is manifested that in the peak $2\theta = 35.20$ again there is a decrease in B and D where there is an increase in samples C and E. CuO impurity phase is

Table 2 Percentage volume fraction of Bi-2223 and Bi-2212 phases in the sample $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$–0.20)

Sample	Mg (x)	Bi-2223 (%)	Bi-2212 (%)
A	0.00	48	52
B	0.05	52	48
C	0.10	54	46
D	0.15	55	45
E	0.20	52	48

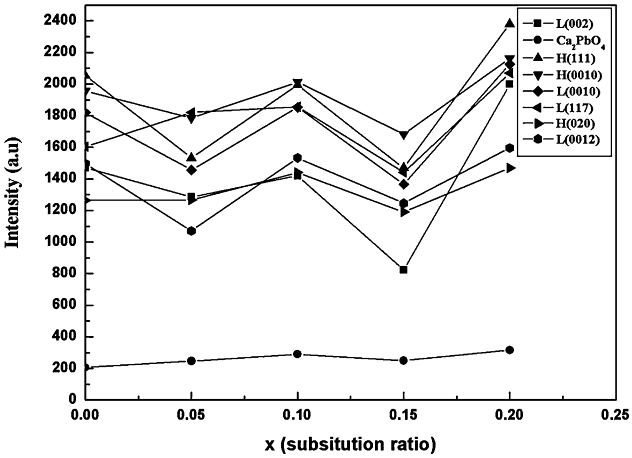

Fig. 4 The change of peak intensities with amount of substitution

not observed in sample A, but it appears in other samples in $2\theta = 30.02$. Its intensity increases in C and E, while it decreases in sample D.

Ca_2PbO_4 impurity phase observe in $2\theta = 17.88$ degree. Its intensity increases in samples B, C, E and decreases in sample D. CuO impurity phase is not seen distinctly.

Lattice parameters we calculated are $a = b = 5.4063$ and $c = 37.072$. They are consistent with the Bi-2223 system's theoretical results ($a = b = 5.419$ and $c = 37.06$) [13].

The volume fraction shows in which ratios high-T_c(2223) and low-T_c(2212) phases are formed. It is calculated by following relations [14]:

$$\Gamma_{2223} = \% \frac{\sum(I_{2223})}{\sum(I_{2212}) + \sum(I_{2223})}$$

$$\Gamma_{2212} = \% \frac{\sum(I_{2212})}{\sum(I_{2212}) + \sum(I_{2223})}$$

We say that depending on the substitution content, there was a little increase in amount of 2223 phase. 2223 phase percentages are 48%, 52%, 54%, 55% and 52% in samples A, B, C, D and E respectively. These values are shown in Table 2. We can see that there is no significant effect on Mg substituted samples from XRD results. Variation of volume fraction percentages of Bi-2223 and Bi-2212 phases is shown in Fig. 5.

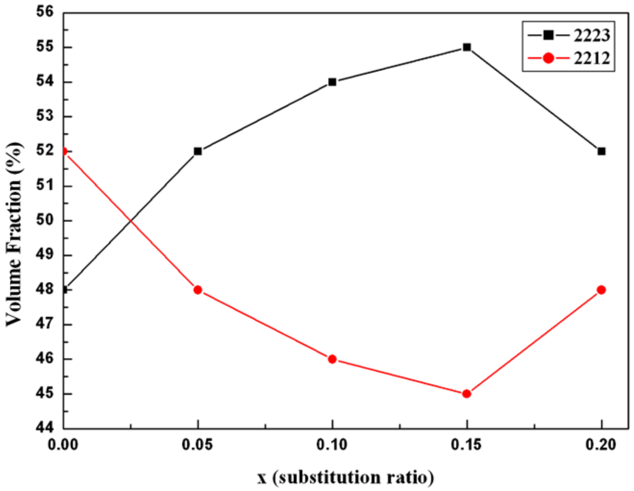

Fig. 5 Variation of volume fraction percentage of Bi-2223 and Bi-2212 phases of Mg doped samples

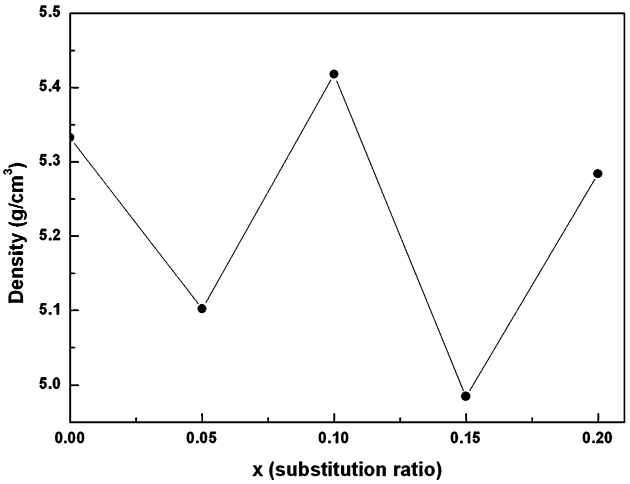

Fig. 6 Variation of densities to Mg content of the samples $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$–0.20)

We determined the densities of samples have different Mg substitutions according to the Archimedes principle by the weight difference between being in pure water and in air. Density is calculated by using the equation

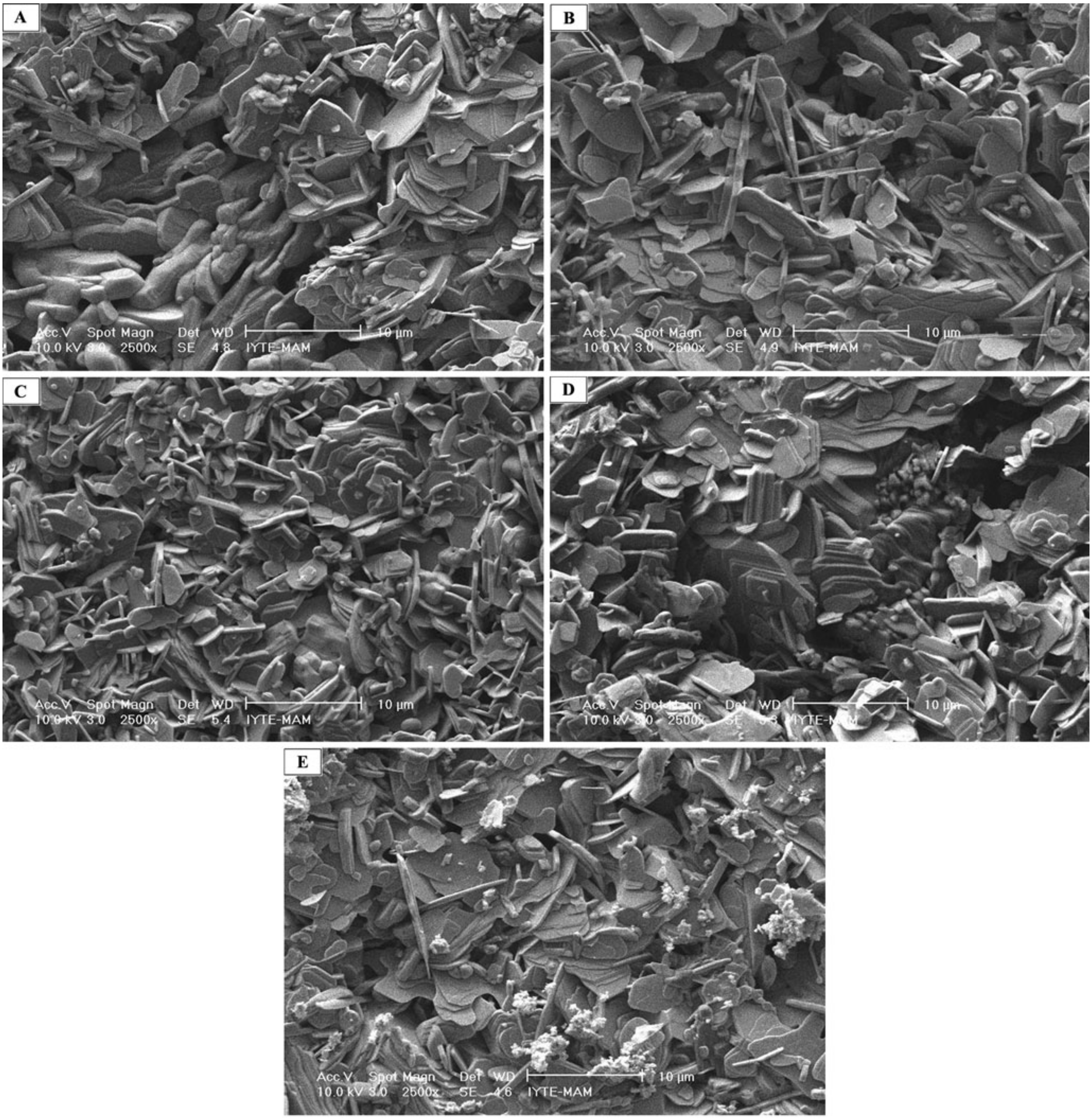

Fig. 7 SEM images of the Mg substituted samples

$$\rho = \frac{W(h)[\rho(s) - \rho(h)]}{0.99983[W(s) - W(h)]} + \rho(h)$$

where $\rho(h)$ and $\rho(s)$ are air and pure water densities and $W(h)$ and $W(s)$ are their weights in these environments sequentially.

Figure 6 shows the change of density depending on the amount of substitution. Densities do not show a linear increase depending on substitution. Densities are 5.3326, 5.1025, 5.4177, 4.9847, 5.2841 $\mathrm{g/cm^3}$ for samples A, B, C, D and E respectively. The theoretical density of BPSCCO system is about 6.3 $\mathrm{g/cm^3}$ as obtained from the lattice parameters [15, 16].

One of the most important properties of high transition temperature in ceramic superconductors is their grained structure. These grained structures can be easily examined by the SEM photographs. In the samples all of the grains headed randomly and grain boundaries seem to be in touch with each other as to make weak bonds. Also this is one of the most characteristic properties of the high-temperature superconductors. The SEM images of the samples are shown in Fig. 7. In the undoped sample, a homogeneous and layered structure was formed. Grains headed randomly and there are voids. In sample B it is examined that homogeneity was deformed in comparison with sample A. Orientation of plate-like structures changed in sample B. In doped sample C, layered structures have been decomposed and grain sizes have gotten smaller. The impurities began to form in sample D and they became dominant in sample E. The presence of MgO influenced the microstructure of the samples and decreased the mean size of Bi-2223 grains up to $x = 0.10$ content.

4 Conclusion

The bulk samples with the nominal composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_{3-x}Mg_xO_y$ ($x = 0.00$, 0.05, 0.10, 0.15 and 0.20) were prepared by a solid-state reaction method. The effect of MgO on the microstructure and superconducting properties of (Bi,Pb)2223 was studied. We can say that MgO addition did not have a significant effect on the formation rate of Bi-2223 phase. Also it influenced the microstructure of the samples and decreased the mean grain size of Bi-2223 grains up to $x = 0.10$. These results are confirmed by XRD, SEM and electrical-resistivity measurements.

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