Effect of La$_{0.7}$Sr$_{0.3}$MnO$_3$ addition on superconducting properties and local structure of (Bi, Pb)-2223 superconductor

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Abstract

The effect of La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) addition on the superconducting property of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$ ((Bi, Pb)-2223) polycrystalline samples was studied. LSMO (0.3 wt.% to 2.0 wt.%) added (Bi, Pb)-2223 samples were prepared by using a solid-state reaction method. The XRD analyses show that as the LSMO addition increases, the volume fraction of the Bi-2223 phase is gradually decreased. The critical temperature (T_c) exhibits a gradual decrease with a single transition as the LSMO amount increases up to 1.0 wt.%, but a further addition of LSMO induces an abrupt decrease of T_c with a dual transition. The analyses on the local structure of the CuO$_2$ plane from the X-ray absorption fine structure (EXAFS) measurements showed that for the samples with low concentration of LSMO up to 1.0 wt.%, the Cu-O bond length and the CuO$_2$ plane ordering do not degrade from the values of pure (Bi, Pb)-2223, while they get worsen with a further increase of LSMO addition. These results open up the possibility of LSMO as artificial pinning centers of the (Bi, Pb)-2223 system for power application.

Keywords: (Bi, Pb)-2223, LSMO, critical temperature, local structure, Cu-O bond

1. INTRODUCTION

The Bi-Sr-Ca-Cu-O (BSCCO) superconductor was discovered in 1988 as the first high-temperature superconductor, its critical temperature above the boiling point of nitrogen, without a rare-earth element. BSCCO shares a two-dimensional layered (perovskite) structure where the superconducting phenomena vary in the CuO$_2$ planes [1]. The BSCCO system contains three phases under a general formula of Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+\delta}$ where n = 1, 2, and 3 corresponding to the number CuO$_2$ layers in a unit cell. Each phase yields a different superconducting transition temperature (T_c) such as T_c ~ 20 K (Bi-2201, n = 1), T_c ~ 80 K (Bi-2212, n = 2), and T_c ~ 105 K (Bi-2223, n = 3) [2, 3]. Among these, the most promising candidate for application is the Bi-2223 phase due to its high transition temperature [4]. However, the fabrication of BSCCO sample with a pure Bi-2223 phase is found to be difficult since the Bi-2212 phase grows prior to the Bi-2223 phase during synthesis. In 1990, Pierre *et al.* reported that the T_c value of the BSCCO system can be enhanced to ~ 110 K by a partial substitution of Pb in Bi site. The new phase is known as the (Bi, Pb)-2223 superconductor [5].

Although partial addition of certain elements to BSCCO is an effective way to improve the superconducting properties, introducing Pb to the Bi site has brought an additional complication such as high brittleness, low charge carrier densities, weak-link between layer, etc. [6]. Based on the problems mentioned, the researchers are still trying to improve the characteristics of (Bi, Pb)-2223 superconductor using various addition materials. As one of the approaches, introducing magnetic materials with a cubic structure such as Fe$_3$O$_4$, NiO, and Co$_3$O$_4$ to (Bi, Pb)-2223 was tried and it is found that the T_c property was not enhanced as well as a worsened grain connectivity in any concentration [7-9]. So far not many researches on the magnetic material addition to the (Bi, Pb)-2223 system have been reported.

La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) is known to be a prominent member of colossal magnetoresistance belonging to the family of typical perovskites oxides with nearly cubic crystal structure [10, 11]. Excellent magnetic and magnetetotransport properties have been reported with a high metal-insulator transition temperature around 369 K [12, 13].

In this paper, we report the effect of LSMO addition on the superconducting properties of (Bi, Pb)-2223 polycrystalline samples. The concentration of LSMO was varied from 0 to 2.0 wt.%. The relation between the superconducting properties and the local structure of the CuO$_2$ plane by varying the LSMO concentration was investigated using extended X-ray absorption fine structure (EXAFS) spectroscopy.

2. EXPERIMENTAL DETAIL

(Bi, Pb)-2223 superconductors were prepared by the conventional solid-state method with an initial stoichiometry of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$. The quantities of high purity chemicals such as Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, and CuO (Aldrich, 99.9%) were weighed and dried at 730 ℃ for 12 hours to reduce moisture. A stoichiometric

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mixture of SrCO$_3$, CaCO$_3$, and CuO was first grinded and calcinated at 920 ℃ for 48 hours to eliminate remainders of carbonates and to produce an oxide with nominal composition of Sr$_2$Ca$_2$Cu$_3$O$_8$ [14]. The resulting powder was added with high purity Bi$_2$O$_3$ and PbO powders followed by an intermediate grinding, then it was pressed into a pellet. The (Bi, Pb)-2223 pellets were calcinated at 880 ℃ for 48 hours. LSMO prepared using La$_2$O$_3$, SrCO$_3$, and MnO$_2$ powders was calcinated at 900 ℃ for 24 hours and sintered at 1200 ℃ for 48 hours.

The LSMO powder with the amount varying from 0.3 wt.% to 2.0 wt.% was mixed with (Bi, Pb)-2223 and sintered at 900 ℃ for 96 hours. According to the amount of LSMO, the samples were labeled as B-Pure, BL03, BL05, BL07, BL10, BL15, and BL20.

Powder X-ray diffraction (XRD, Cu K$_\alpha$) measurements were carried out to determine the volume fractions of Bi-2223 and Bi-2212 phases. Surface morphology and element composition distribution of the samples were examined using scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. The superconducting transition temperature was measured by using a four-probe technique in a closed cycle refrigerator [15]. The local structure of the Cu-O bonds in the CuO$_2$ plane was investigated by analyzing EXAFS spectra collected in Pohang Accelerator Laboratory (PAL) 8C beam line at room temperature. The collected Cu K-edge spectra were normalized by the ATHENA code followed by the analyses of the bond distance in the 1st Cu-O shell using the ARTEMIS codes of the IFEFFIT (Newville, 2001) software program.

3. RESULT AND DISCUSSION

The influence of LSMO addition on the volume fraction of Bi-2223 phase was extensively studied by XRD measurements. Figure 1 displays the XRD patterns of LSMO added (Bi, Pb)-2223 samples. The formation of Bi-2223 and Bi-2212 phases were verified through peak

matching and are labelled as O and X for Bi-2223 and Bi-2212, respectively. The XRD intensities can be used to calculate relative volume fraction of the Bi-2223 and the Bi-2212 phases by using the following equations (1);

$$Bi-2223 = \frac{\Sigma I(2223)}{\Sigma I(2223) + \Sigma I(2212)} \times 100\%$$

$$Bi-2212 = \frac{\Sigma I(2212)}{\Sigma I(2223) + \Sigma I(2212)} \times 100\%$$

(1)

where I is the phase peak intensity.

The calculated volume fractions of Bi-2223 and Bi-2212 phases, and the lattice parameters are listed in Table I. B-Pure sample possess the highest Bi-2223 phase. As the LSMO addition increases up to 1.0 wt.%, the Bi-2223 phase gradually decreases from 72.5 % to 70.2 %, while the LSMO addition further increases to 2.0 wt.%, the Bi-2223 phase abruptly decreases to 63.8 %. On the other hand, both the *ab*-plane and the *c*-axis parameters are nearly constant with increasing the LSMO addition. This result combined with no additional secondary phase observed up to 2.0 wt.% indicate that the added LSMO does not go into the crystal structure of BSCCO system. Similar results of unchanged peak positions and undetected impurities have been reported in the addition of Bi$_2$Te$_3$ [16], Al$_2$O$_3$ [17], AgCO$_3$ [18], and Eu$_2$O$_3$ [19] to the BSCCO system.

The elemental compositions of the samples were quantitatively determined by using energy dispersive X-ray spectroscopy (EDS) measurements as shown in Fig. 2.

TABLE I
Volume fractions of (Bi, Pb)-2223 and lattice parameters with LSMO addition

Sample	Volume Fraction (%)		Lattice Parameter (Å)	
	2223	2212	*ab*-plane	*c*-axis
B-Pure	72.5	27.5	5.41	37.27
BL03	70.6	29.4	5.40	37.24
BL05	70.5	29.5	5.40	37.25
BL07	70.3	29.7	5.41	37.26
BL10	70.2	29.8	5.40	37.26
BL15	68.6	31.4	5.40	37.25
BL20	67.8	32.2	5.40	37.26

Fig. 2. The EDS spectra of LSMO 2 wt.%-added (Bi, Pb)-2223 sample at different of regions of (a) granular and (b) platelike-grain.
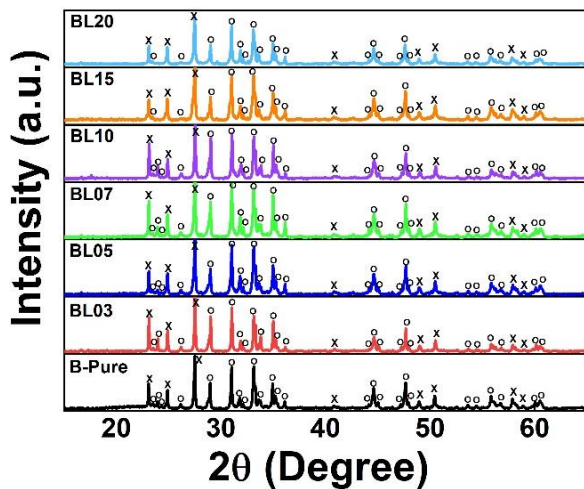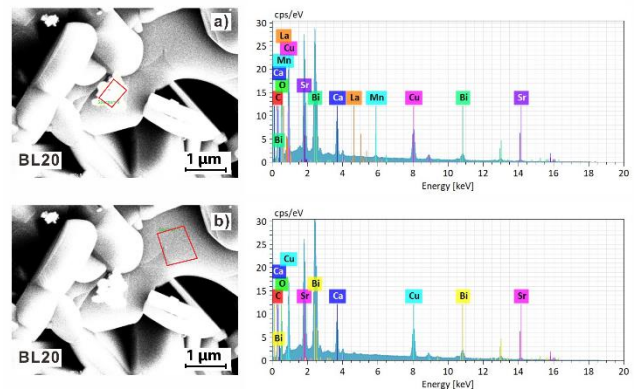

Fig. 1. XRD patterns of (Bi, Pb)-2223 samples with LSMO addition from 0.3 wt.% to 2.0 wt.%. Bi-2223 and Bi-2212 phases are marked with O and X, respectively.
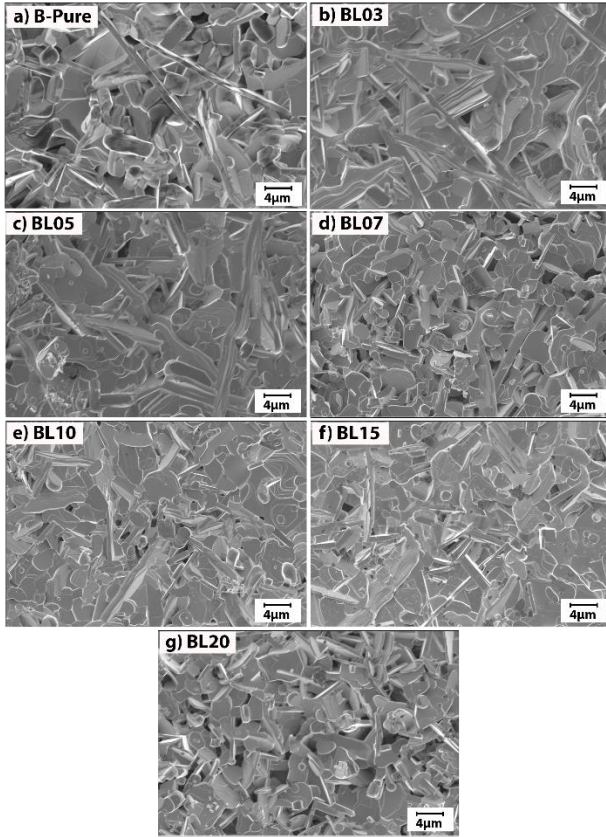
Fig. 3. SEM micrographs of (Bi, Pb)-2223 with various LSMO concentrations from 0.3 wt.% to 2.0 wt.% compared with that of pure (Bi, Pb)-2223.

It is observed that LSMO is mainly embedded in the grain boundaries as granular in BL20.

The surface morphologies of the samples are represented in Figs. 3(a) to (g). B-pure sample shows a distribution of random alignment of platelike-grains, a signature of the formation of Bi-2223 phase [20]. The morphology of the grains does not significantly change with the LSMO concentration up to 1.5 wt.%, which confirms that low porosity and good intergrain connectivity between superconducting grains are maintained with a certain amount of LSMO addition. As the LSMO concentration increases to 2.0 wt.%, the surface morphology degrades as the number of pores increases and grain connectivity gets worse.

The electrical resistances of all samples as a function of temperature are plotted in Fig. 4. As can be seen, all samples exhibit a well-defined metallic-like behavior at normal state followed by a transition to the superconducting state. It is clear that the superconducting transition gets broadened with increasing LSMO addition and a dual transition is appeared in BL20, which may be due to a considerable increase of the Bi-2212 phase.

Figure 5(a) shows the values of T_c as a function of LSMO concentration, determined from the temperatures corresponding to the maximum dR/dT. The highest T_c of 106.6 K belongs to B-pure sample and the T_c values show a tendency of decrease with the LSMO concentration except for BL10 sample of which T_c value increases. BL20 with a maximum LSMO concentration shows a dual
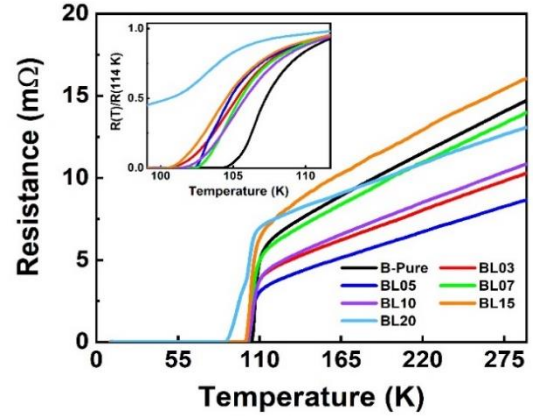

Fig. 4. Electrical resistances of (Bi, Pb)-2223 samples with various LSMO concentration as a function of temperature. Inset: Magnified view of the superconducting transition.

transition of 103.23 K for T_{c1} and 94.76 K for T_{c2}. Furthermore, little fluctuation and a sudden decrease beyond 1.0 wt.% of the residual resistance ratio (RRR) as well as an opposite behavior of the superconducting transition ΔT_c with increasing LSMO concentration are observed as depicted in Fig. 5(b). ΔT_c were obtained from the full-width at half-maximum of the fitting process shown in the inset of Fig. 5(a) [21, 22]. These results may be attributed to an increase of Bi-2212 phase by the addition of LSMO supported by the XRD analyses [23].

In order to understand the T_c behavior with the LSMO addition, EXAFS measurements, an ideal tool to measure the distribution of atomic displacement, were conducted. Figure 6 shows the Fourier transform (FT) of the EXAFS signals extracted from the Cu K-edge absorption spectra of (Bi, Pb)-2223 samples with various LSMO concentration. The transform window was set to be $k = (3.0 – 10.5)$ Å^{-1}. The first shell (1st shell), which corresponds to the contribution of the Cu-O scatterings, is located at ~1.45 Å.
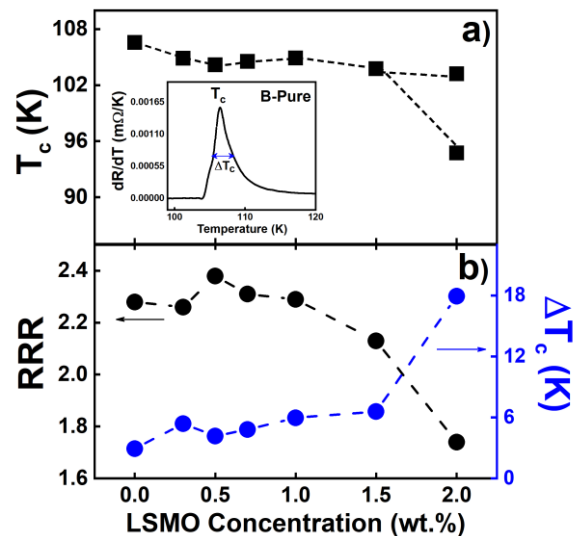

Fig. 5. (a) T_c as a function of LSMO concentration. Inset: determination of T_c and ΔT_c from dR/dT (b) Residual resistance ratio (RRR) and ΔT_c as a function of LSMO concentration.
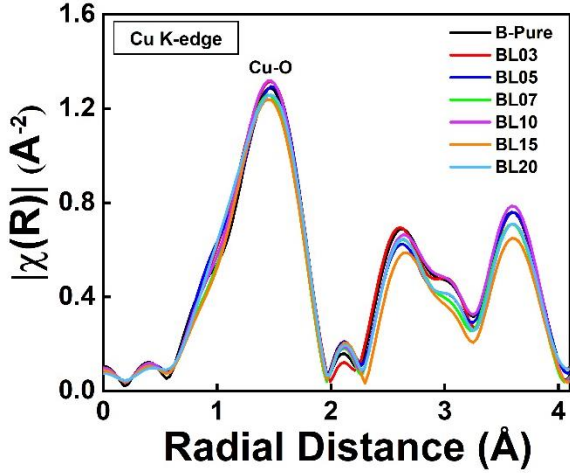
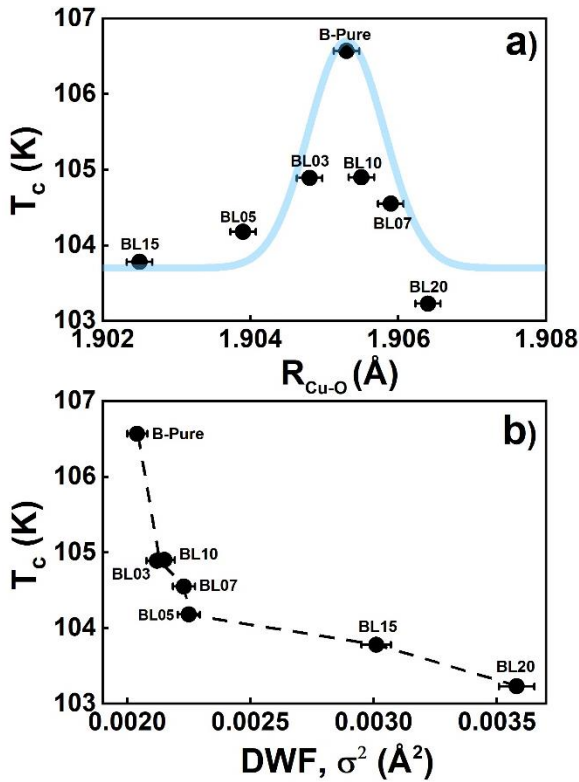Fig. 6. Fourier transforms of Cu K-edge EXAFS spectra of (Bi, Pb)-2223 samples with various LSMO addition.

Fig. 7. The correlation of the transition temperature with (a) the Cu-O bond distance (R) and (b) the Debye-Waller factor (DWF) of the Cu-O pair.

Because the peak positions in FT do not represent the real atomic distance, the 1st shell fitting was carried out to find the quantitative values of the atomic position with respect to the Cu atom. During the fitting process, only two parameters, the Cu-O bond length (R) and the Debye-Waller factor (DWF), were allowed to vary and other parameters were fixed.

Figures 7(a) and (b) show the variation of the Cu-O bond length and the Debye-Waller factor (DWF) with various LSMO concentration obtained from the fitting. Our EXAFS analyses show a close relation between T_c and the

Cu-O bond length, which has been reported in other cuprates [24-26]. The distribution of T_c values as a function of the Cu-O bond length represents a Gaussian-like function, and an optimum bond length of B-pure sample with the highest T_c is around 1.905 Å. Most samples with low LSMO concentration are located near the optimum bond length. As the LSMO concentration further increases such as in BL15 and BL20, the Cu-O bond lengths deviate from the optimal value. In addition, a large compression/elongation of the Cu-O bond results in a distortion in the CuO$_2$ plane manifested as an abrupt increase of the DWF values, which explain the degraded T_c values observed in BL15 and BL20. Therefore, it can be concluded that the LSMO addition up to 1.0 wt.% can preserve the superconducting properties of (Bi, Pb)-2223 samples by maintaining the Bi-2223 volume fraction and stability of the CuO$_2$ plane.

4. CONCLUSION

The effect of LSMO addition from 0 to 2.0 wt. % to (Bi, Pb)-2223 polycrystalline superconductor was investigated. The analysis of X-ray diffraction data indicates that the volume fraction of Bi-2223 phase gradually decreases as the LSMO addition increases up to 1.0 wt.%, and then abruptly decreases with a further increase of LSMO concentration. The superconducting properties such as T_c and the superconducting transition were also gradually degraded with LSMO addition, and the R-T curve of LSMO 2 wt.% sample shows a dual transition indicating a considerable amount of the Bi-2212 phase.

The EXAFS measurements at the Cu K-edge were carried out to identify the effect of LSMO on the local structure of the (Bi, Pb)-2223 system. The LSMO addition up to 1.0 wt.% does not cause to significantly change the Cu-O bond distance as well as the DWF values, therefore the superconducting properties can be maintained. On the other hand, heavier addition of LSMO is found to cause the suppression/elongation of Cu-O bond and the distortion in the CuO$_2$ plane due to an increase of the Bi-2212 phase. These results help to find a possible candidate for artificial pinning centers for the (Bi, Pb)-2223 system from an application point of view.

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