

# Influence of $\text{Sr}(\text{BO}_2)_2$ Doping on Superconducting Properties of (Bi,Pb)-2223 Phase

N. G. Margiani, I. G. Kvartskhava, G. A. Mumladze, Z. A. Adamia

**Abstract**—Chemical doping with different elements and compounds at various amounts represents the most suitable approach to improve the superconducting properties of bismuth-based superconductors for technological applications. In this paper, the influence of partial substitution of  $\text{Sr}(\text{BO}_2)_2$  for SrO on the phase formation kinetics and transport properties of (Bi,Pb)-2223 HTS has been studied for the first time. Samples with nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$ ,  $x=0, 0.0375, 0.075, 0.15, 0.25$ , were prepared by the standard solid state processing. The appropriate mixtures were calcined at  $845^\circ\text{C}$  for 40 h. The resulting materials were pressed into pellets and annealed at  $837^\circ\text{C}$  for 30 h in air. Superconducting properties of undoped (reference) and  $\text{Sr}(\text{BO}_2)_2$ -doped (Bi,Pb)-2223 compounds were investigated through X-ray diffraction (XRD), resistivity ( $\rho$ ) and transport critical current density ( $J_c$ ) measurements. The surface morphology changes in the prepared samples were examined by scanning electron microscope (SEM). XRD and  $J_c$  studies have shown that the low level  $\text{Sr}(\text{BO}_2)_2$  doping ( $x=0.0375$ - $0.075$ ) to the Sr-site promotes the formation of high- $T_c$  phase and leads to the enhancement of current carrying capacity in (Bi,Pb)-2223 HTS. The doped sample with  $x=0.0375$  has the best performance compared to other prepared samples. The estimated volume fraction of (Bi,Pb)-2223 phase increases from ~25 % for reference specimen to ~70 % for  $x=0.0375$ . Moreover, strong increase in the self-field  $J_c$  value was observed for this dopant amount ( $J_c=340\text{ A/cm}^2$ ), compared to an undoped sample ( $J_c=110\text{ A/cm}^2$ ). Pronounced enhancement of superconducting properties of (Bi,Pb)-2223 superconductor can be attributed to the acceleration of high- $T_c$  phase formation as well as the improvement of inter-grain connectivity by small amounts of  $\text{Sr}(\text{BO}_2)_2$  dopant.

**Keywords**—Bismuth-based superconductor, critical current density, phase formation,  $\text{Sr}(\text{BO}_2)_2$  doping.

## I. INTRODUCTION

SINCE the discovery of  $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y$  (Bi-2223) HTS, it has been considered to be one of the most attractive superconducting materials for large scale technological applications [1]. However, due to the very slow formation kinetics of the Bi-2223 phase, long heat-treatment times measured in hundreds of hours are usually required to prepare nearly single-phase Bi-2223 HTS in the final product [2]. Many factors, including the nominal composition of the precursor powder, thermal processing time and temperature, particle size of dopants, milling treatment of precursor, texturing and synthesis atmosphere significantly influence the

phase formation kinetics and  $J_c$  of Bi-2223 HTS [3], [4]. Doping studies have demonstrated that substitution or addition of micro - and nanosized dopants is an efficient method to promote the high- $T_c$  phase formation, as well as to improve the intergrain connectivity and flux pinning capability in Bi-2223 system [5]-[9].

Our previous results show that the doping with lead borate ( $\text{Pb}(\text{BO}_2)_2$ ), boron nitride (BN) and boron carbide ( $\text{B}_4\text{C}$ ) promotes the formation of (Bi,Pb)-2223 phase and leads to the enhancement of transport properties compared to the reference sample [10]-[12]. The effects of strontium borate [ $\text{Sr}(\text{BO}_2)_2$ ] doping on the formation and superconducting properties of (Bi,Pb)-2223 system have not yet reported. Hence, the purpose of this research is to investigate whether the partial substitution of  $\text{Sr}(\text{BO}_2)_2$  for SrO has a similar positive effect on the superconducting properties of (Bi,Pb)-2223 ceramics.

## II. MATERIALS AND METHODS

Samples with nominal composition  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$ ,  $x=0, 0.0375, 0.075, 0.15, 0.25$  (0, 0.63, 1.3, 2.5, 4.2 wt % of  $\text{Sr}(\text{BO}_2)_2$ , respectively) were prepared by the solid state reaction method. Appropriate amounts of highly pure  $\text{Bi}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ ,  $\text{CuO}$  and  $\text{Sr}(\text{BO}_2)_2$  chemical powders were mixed and sintered at  $845^\circ\text{C}$  for 40 h in air with intermediate manual grindings using agate mortar and pestle. The resulting materials were pressed into pellets of 10 mm in diameter and 1.5 mm thickness under hydrostatic pressure of 29 MPa. The pellets were annealed at  $837^\circ\text{C}$  for 30 h in air, then cooled to room temperature in the furnace. The synthesized compounds were characterized by powder XRD analysis using the Dron-3M diffractometer ( $\text{CuK}_\alpha$  radiation). The resistivity as a function of temperature,  $\rho(T)$ , and transport critical current density,  $J_c$ , were measured by a standard four-probe method. The surface morphology of the samples was examined using a SEM (VEGA TS5130MM). The DC current of 5 mA was applied to determine the  $\rho(T)$  dependence of the samples. The typical sample size for measurements of critical current density was  $\sim 9\text{ mm} \times 0.5\text{ mm} \times 0.5\text{ mm}$ .  $J_c$  values of prepared samples were measured at the liquid nitrogen temperature in the self-field, using a criterion of  $1\text{ }\mu\text{V/cm}$ .

## III. RESULTS AND DISCUSSIONS

XRD patterns of the reference and  $\text{Sr}(\text{BO}_2)_2$ -doped compositions are shown in Fig. 1. The dominance of the low- $T_c$  2212 phase over the high- $T_c$  2223 phase was observed in the reference sample.  $\text{Sr}(\text{BO}_2)_2$ -doping leads to the enhancement of the high- $T_c$  2223 phase, whereas the intensity

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of the 2212 peaks decreases. The Bi-2201 phase with  $T_c \approx 20$  K appears at doping level of  $x=0.15$  and intensifies with increasing a dopant content to  $x=0.25$ . Moreover, XRD pattern for  $x=0.25$  shows a broad diffuse halo indicating the deterioration of crystallinity for the high doping level.

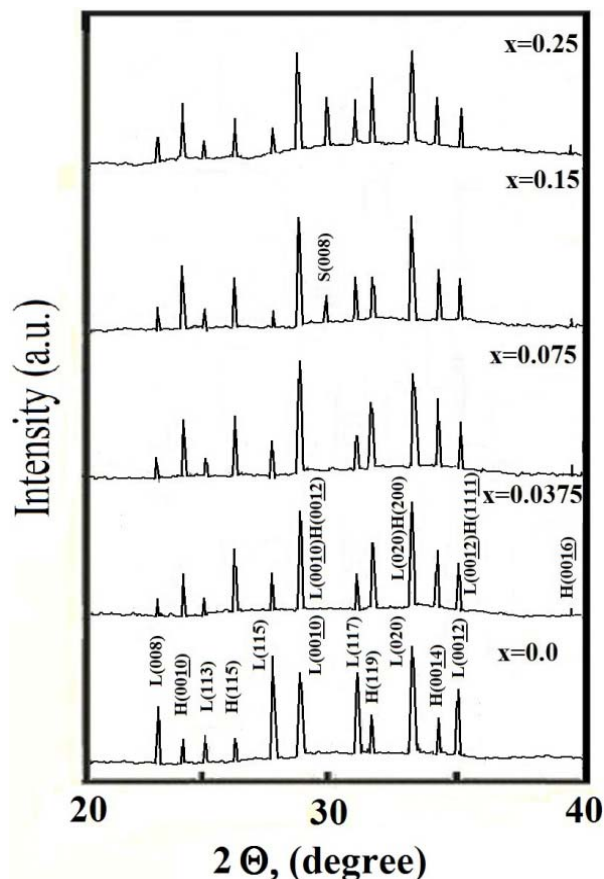


Fig. 1 XRD patterns of  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$  samples. The diffraction peaks indexed H(hkl), L(hkl) and S(hkl) represent the Bi-based 2223, 2212 and 2201 phases, respectively

The volume fractions (V) of the (Bi,Pb)-2223 phase were estimated from XRD intensity ratios of the (Bi,Pb)-2223 and Bi-2212 phases using the following equation [13]:  $V = \{I_{\text{H}(0010)} / [I_{\text{H}(0010)} + I_{\text{L}(008)}]\} \times 100$  [%], where  $I_{\text{H}(0010)}$  is the XRD peak intensity of (0010) in the Bi-2223 phase and  $I_{\text{L}(008)}$  is the peak intensity of (008) in the Bi-2212 phase. The calculated volume fraction of (Bi,Pb)-2223 phase increases from ~25 % for reference specimen to ~70 % for  $x=0.0375$  in a relatively short sintering time of 70 h, which indicates that  $\text{Sr}(\text{BO}_2)_2$  dopant accelerates the solid state reaction rate and hence the (Bi,Pb)-2223 formation. Structural role of boron additives in Bi(Pb)-2223 is not clear at present. In our previous studies of the BN and  $\text{B}_2\text{O}_3$ -doping effects on Bi(Pb)-Sr-Ca-Cu-O superconductor properties, we assumed that due to their extremely small ionic radius, doped  $\text{B}^{3+}$  ions may occupy interstitial positions in the lattice and alter the charge carrier concentration [11], [14]. Overdoping can cause a transition to the amorphous glassy structure [15].

The linear temperature dependence of the resistivity in the

normal state region was observed for all the samples. Onset temperature of superconducting transition is about 115 K for the reference sample and remains unchanged with the  $\text{Sr}(\text{BO}_2)_2$ -doping. For the undoped specimen, zero resistivity is reached at  $T_c^{\text{off}}=104$  K.  $T_c^{\text{off}}$  decreases to 103 K with the  $\text{Sr}(\text{BO}_2)_2$  content of  $x=0.0375$ . A further addition of  $\text{Sr}(\text{BO}_2)_2$  leads to gradual decrease of  $T_c^{\text{off}}$  values, probably due to formation of the Bi-2201 phase with  $T_c \approx 20$  K. Fig. 3 illustrates the relationship between the transport  $J_c$  values (77 K, zero field) and the amount of  $\text{Sr}(\text{BO}_2)_2$  dopant.

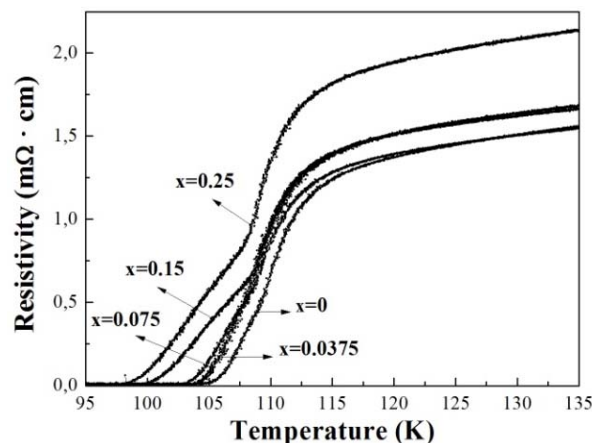


Fig. 2 Resistivity versus temperature curves for  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$  samples

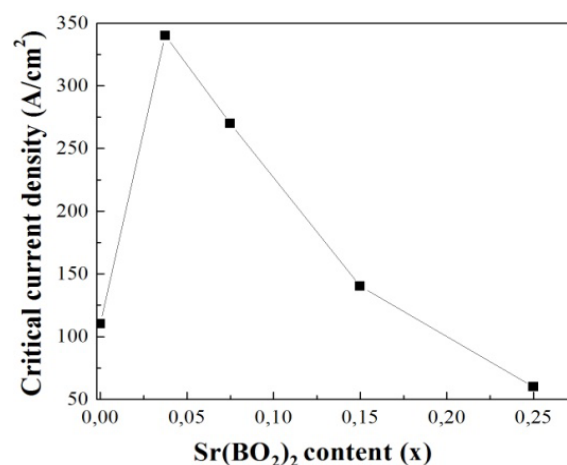


Fig. 3 Relationship between the critical current density and  $\text{Sr}(\text{BO}_2)_2$  content in  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$  samples

The value of  $J_c$  is 110  $\text{A}/\text{cm}^2$  for reference sample, which is consistent with the literature values for bulk, non-textured (Bi,Pb)-2223 superconductors [16]. Significantly enhanced  $J_c$  values were observed for the  $\text{Sr}(\text{BO}_2)_2$ -doped samples ( $x=0.0375 - 0.075$ ), especially with  $x=0.0375$  ( $J_c=340$   $\text{A}/\text{cm}^2$ ). This  $J_c$  value is about 3 times higher than that of the reference compound processed for the same total sintering time of 70 h. Enhancement of critical current density seems to result from the increase of the (Bi,Pb)-2223 volume fraction and improvement of the intergrain coupling in  $\text{Sr}(\text{BO}_2)_2$ -doped sample. In agreement with the XRD and resistivity data shown

in Figs. 1 and 2, decrease of  $J_c$  values for a higher level of  $\text{Sr}(\text{BO}_2)_2$ -doping ( $x > 0.075$ ) implies the worsening of coupling at grain boundaries due to formation of 2201 phase and marked deterioration of the crystallinity for  $x = 0.25$ .

Fig. 4 illustrates the surface SEM micrographs of the reference and  $\text{Sr}(\text{BO}_2)_2$ -doped samples under an identical

magnification of 5000 $\times$ . The sample with  $x = 0.0375$  has more oriented and dense plate-like microstructure compared to the samples with  $x = 0$  and 0.25. Stronger contacts between superconducting grains promotes the improvement of current carrying capability of doped (Bi,Pb)-2223 at  $x = 0.0375$ .

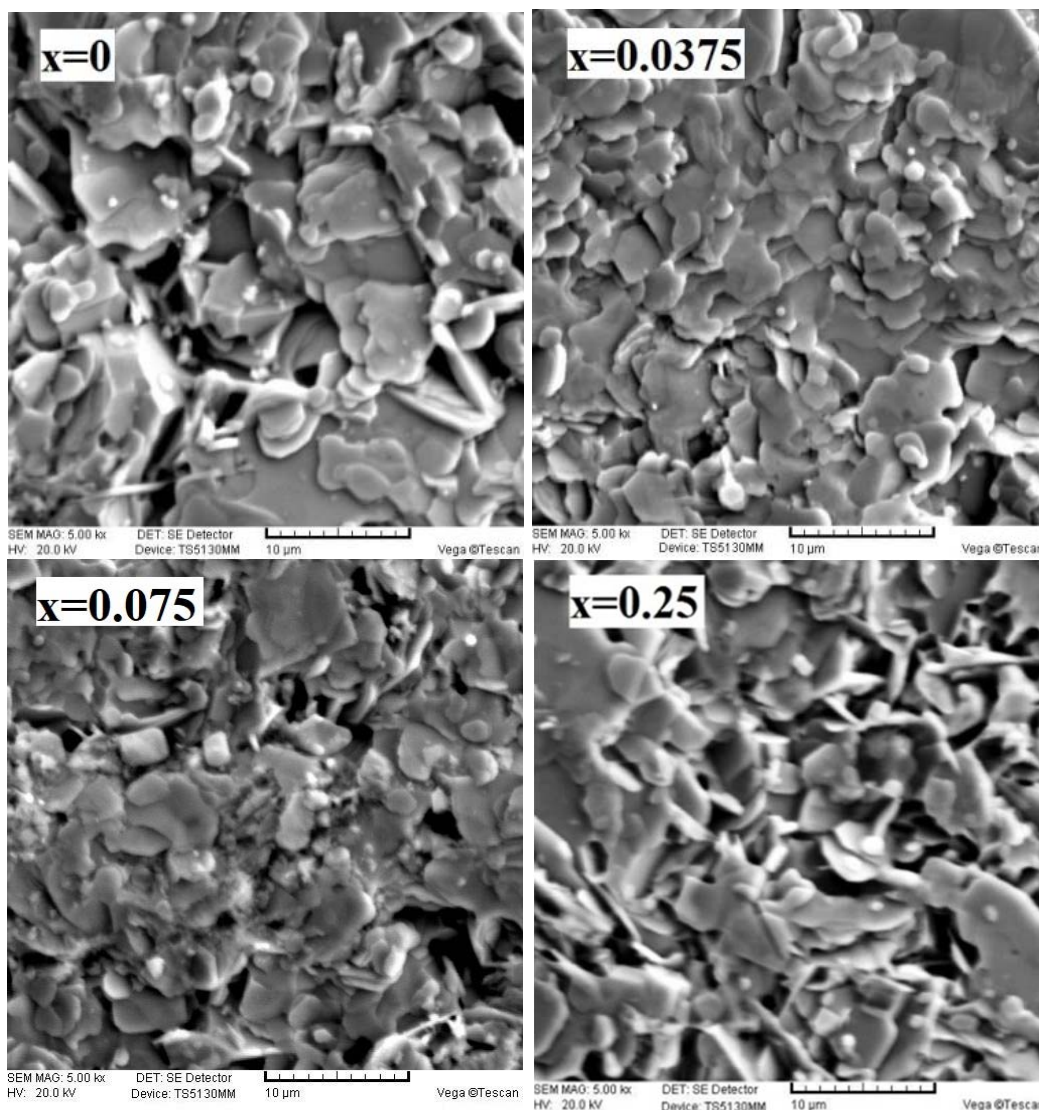


Fig. 4 Surface SEM images of the  $\text{Bi}_{1.7}\text{Pb}_{0.3}\text{Sr}_{2-x}\text{Ca}_2\text{Cu}_3\text{O}_y[\text{Sr}(\text{BO}_2)_2]_x$  samples

#### IV. CONCLUSIONS

The preliminary results obtained in this study suggest that the  $\text{Sr}(\text{BO}_2)_2$  has to be considered as a suitable dopant for enhancing the formation kinetics and transport properties of (Bi,Pb)-2223 HTS. The critical current density of Bi-based system was strongly enhanced due to the introduction of  $\text{Sr}(\text{BO}_2)_2$  dopant up to 1.3 wt.%. The superconducting properties of the  $\text{Sr}(\text{BO}_2)_2$ -doped (Bi,Pb)-2223 compositions are still not optimized. It is therefore interesting to search for the best doping level and optimum processing conditions providing formation of larger fraction of the high- $T_c$  phase and further enhancement of critical current density in  $\text{Sr}(\text{BO}_2)_2$ -

doped (Bi,Pb)-2223 system. This problem is under our investigation. Also, future study of the subject can involve the impact of high energy planetary ball milling on the microstructure, phase formation and transport properties of  $\text{Sr}(\text{BO}_2)_2$ -doped (Bi,Pb)-2223 HTS

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