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Physics

On the Structural Characteristics of the B_4C-Doped Bi(Pb)-2223 Superconductor

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(Presented by Academy Member Anzor Khelashvili)

The present paper reports on the impact of boron carbide (B4C) additive on phase formation and physical properties of Bi(Pb)-2223 high-temperature superconductor (HTS). Refe-rence and B4C-added Bi(Pb)-2223 samples with nominal composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y(B_4C)_x$, x=0, 0.040 and 0.075 were prepared by solid-state reaction method. Precursor powders were manually grinded in agate mortar and sintered at 850^{0}C for 30 hours with intermediate grindings; obtained materials were pressed into pellets and annealed at 845^{0}C for 40 hours, then cooled to room temperature in the furnace. The evolution of Bi(Pb)-2223 phase in prepared samples was investigated by X-ray diffraction (XRD) analysis and volume fraction of Bi(Pb)-2223 phase was estimated from XRD data. The lattice parameters for Bi(Pb)-2223 phase were calculated from XRD patterns. The temperature dependence of electrical resistivity $\rho(T)$ was measured by four-probe method. Transmission electron microscope (TEM) and scanning transmission electron Microscope (STEM) were used for microstructural and elemental analysis of synthesized samples. The $\rho(T)$ dependences show a two-step superconducting transition with T_c>100 K, indicating the coexistence of high-Tc 2223 and low-Tc 2212 phases in prepared materials. XRD analysis confirms that B_4C-doping leads to the marked enhancement of Bi(Pb)-2223 phase volume fraction from 56% for un-doped sample up to 88% at x=0.04. Gradual decrease of lattice parameters with increasing doping level can be attributed to the partial substitution of B^{3+} ions for Cu^{2+} ions. The areas with completely formed, partly formed and unformed Bi(Pb)-2223 phase have been visually revealed by the TEM/STEM imaging and elemental analysis. *© 2020 Bull. Georg. Natl. Acad. Sci.*

Bi(Pb)-2223 superconductor, doping, phase formation, structure, TEM mapping

Since the discovery of $Bi_2Sr_2Ca_2Cu_3O_y$ (Bi(Pb)-2223) high-temperature superconductor (HTS) [1], it has been considered to be one of the most promising materials for large scale applications in superconducting industry, especially for the producing of superconducting wires due to its best texturing ability. However, due to a very slow formation rate, fabrication of the nearly pure Bi(Pb)-2223 phase is a time-consuming process and hundreds of hours are needed to synthesize an appropriate fraction of Bi(Pb)-2223 HTS in the final product [2]. Partial substitution of Bi by Pb is the most practical method of enhancing the Bi(Pb)-2223 fraction [3]. Micro, sub-micro and nano-sized dopants have been widely used in order to accelerate Bi(Pb)-2223 phase formation and increase the critical current density (Jc). In our previous investigations we have shown that the boron-containing additives, such as B_2O_3, BN, B, $Pb(BO_2)_2$, B_4C and $Sr(BO_2)_2$ lead to a significant acceleration of Bi(Pb)-2223 phase formation and enhancement of transport critical current density [4-10]. In this work, we focus on the structural role of boron carbide additive in Bi(Pb)-2223 along with the transmission electron microscopy (TEM) imaging and elemental analysis of prepared Bi(Pb)-2223 ceramics.

Materials and Methods

Samples with nominal composition $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y(B_4C)x$, x=0, 0.040 and 0.075, were prepared from the appropriate amounts of highly pure Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO and B_4C (Sigma-Aldrich product) precursors by conventional solid-state reaction method. A mix of precursor powders was manually grinded in agate mortar and sintered at 850^0C for 30 hours with intermediate manual grindings; obtained materials were pressed into pellets with 10 mm in diameter and up to 2 mm thickness under pressure of 300 MPa. Pellets were annealed at 845^0C for 40 hours, then cooled to room temperature in the furnace. Prepared samples were characterized by x-ray diffraction (XRD) analysis using the Bruker D8 Discover diffractometer. Evolution of Bi(Pb)-2223, Bi-2212, Bi-2201 and other phases with increasing doping level were revealed and lattice parameters (a, b, c) of Bi(Pb)-2223 were calculated from XRD data for all the prepared samples. The resistivity as a function of temperature, $\rho(T)$, was measured by a standard four-probe method. The TEM/STEM analysis was performed using the Thermo Fisher Scientific S/TEM with 4 Si drift EDS detectors and sample morphology and elemental analysis were performed in order to reveal completed solid-state reaction (wide-scale regions of Bi(Pb)-2223 phase), non-reacted or poorly formed superconducting areas.

Results and Discussion

XRD patterns of reference and B_4C-doped samples are presented in the Fig.1. Addition of B_4C leads to the increase of 2223 phase peaks (indicated as H), whereas the intensity of low-Tc 2212 phase (indicated as L) decreased.

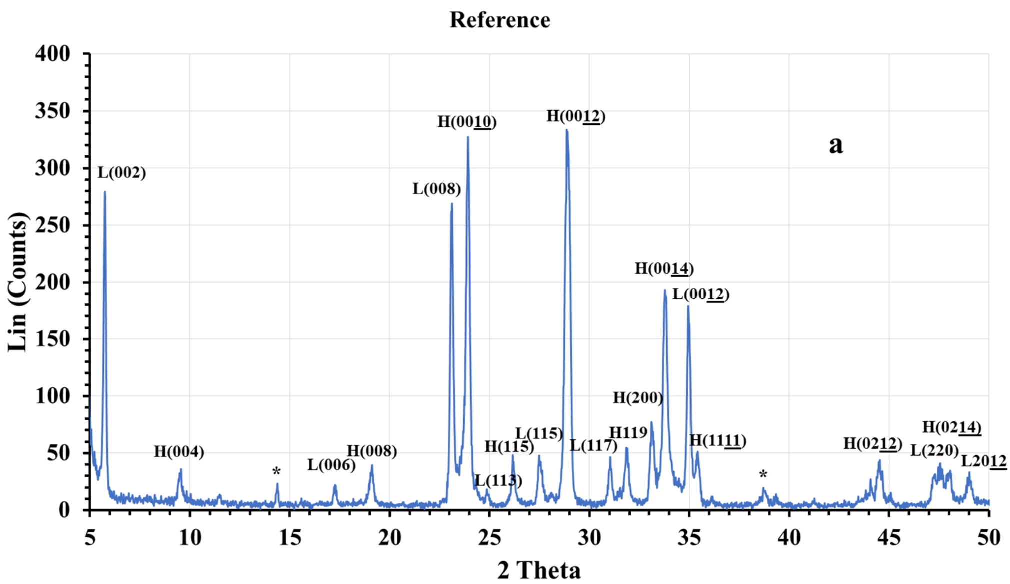

Fig. 1. The XRD patterns of selected samples: a – reference sample (x=0).

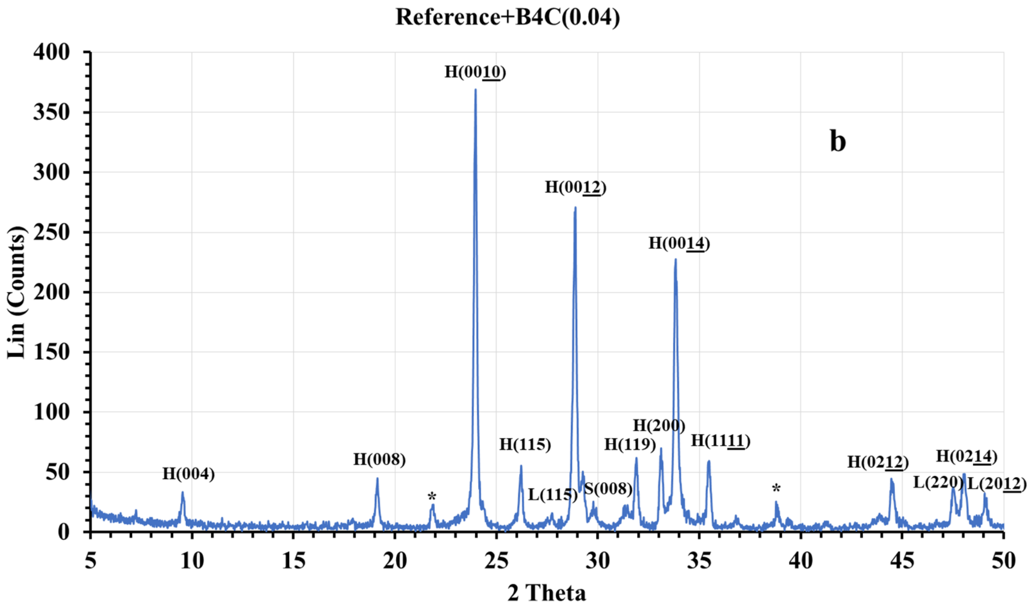

Fig. 2. The XRD patterns of selected samples: b – doped with B_4C (x=0.04).

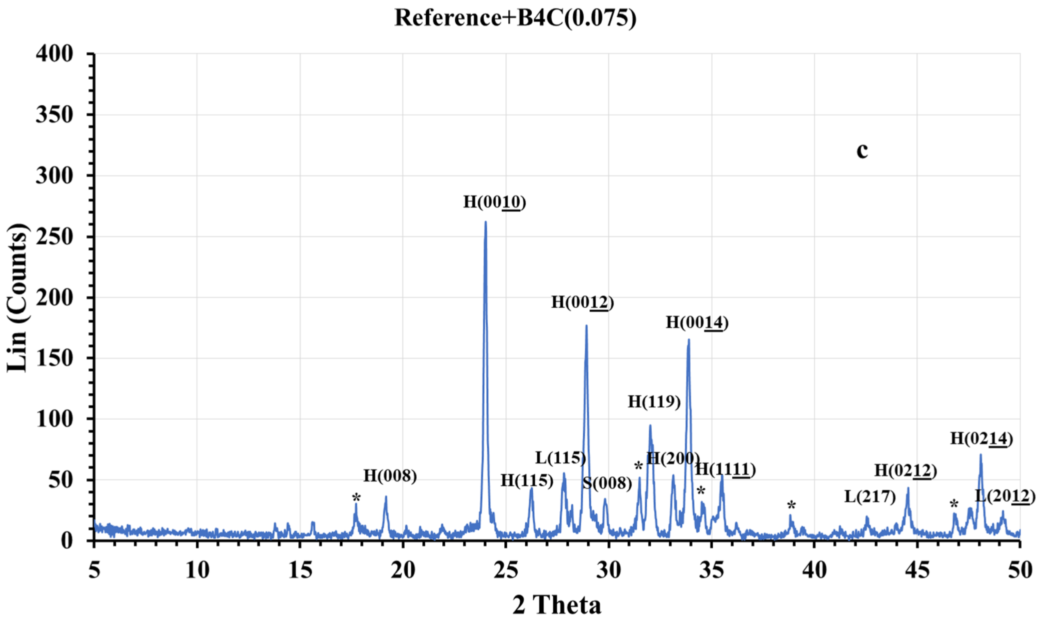

Fig. 3. The XRD patterns of selected samples: c – doped with B_4C (x=0.075).

The volume fraction (V) of the Bi(Pb)-2223 phase was estimated from XRD data using the following equation [11]:

$$V(2223\%) = \frac{\sum I(H)}{\sum I(H) + \sum I(L) + \sum I(others)} \times 100, \qquad (1)$$

where I(H), I(L) and I(others) are the intensities of the XRD peaks of 2223, 2212 and other phases, respectively. Volume fraction of Bi(Pb)-2223 HTS phase increases from 56% for un-doped sample up to 88% for x=0.04 and then decreases to 78% for x=0.075. These results agree with those obtained in our previous works [4-10]. In Fig. 2 resistivity versus temperature curves are displayed for synthesized samples. The *ρ(T)* dependences show a two-step superconducting transition, indicating the coexistence of 2223 and 2212 phases in prepared materials. For the un-doped specimen zero resistivity is reached at Tc=102.5K. Critical temperature decreases slightly to 101.5K at x=0.040 and 100K at x=0.075.

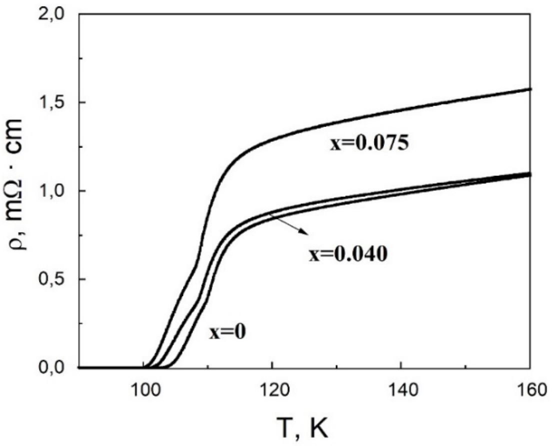

Fig. 4. Resistivity vs temperature dependence for reference and B_4C doped samples.

The lattice parameters a, b, c were calculated for reference and B_4C-added samples (Table 1). Obtained results indicate that doping causes a decrease of these parameters, suggesting a partial substitution of B^{3+} ions (ionic radii ~0.23 Å) for Cu^{2+} ions (ionic radii ~0.83 Å) in Cu–O layers, as for the case of B_2O_3-added Tl-2212 and Tl-2223 superconductors [12]:

Table 1. Lattice parameters of reference and B_4C-added samples, Å

	Ref	Ref+B_4C(0.04)	Ref+B_4C(0.075)
a	5.41784	5.40315	5.40248
b	5.46687	5.42127	5.41054
c	37.21183	37.06498	37.05159

For the first time in our researches, TEM/STEM analysis was employed for imaging in selected areas and the painstaking elemental analysis was carried out as well. The results of TEM/STEM analysis are shown in Fig. 3. Areas 1, 2 and 3 were revealed, indicating the completely formed, partly formed and unformed Bi(Pb)-2223 phase, respectively.

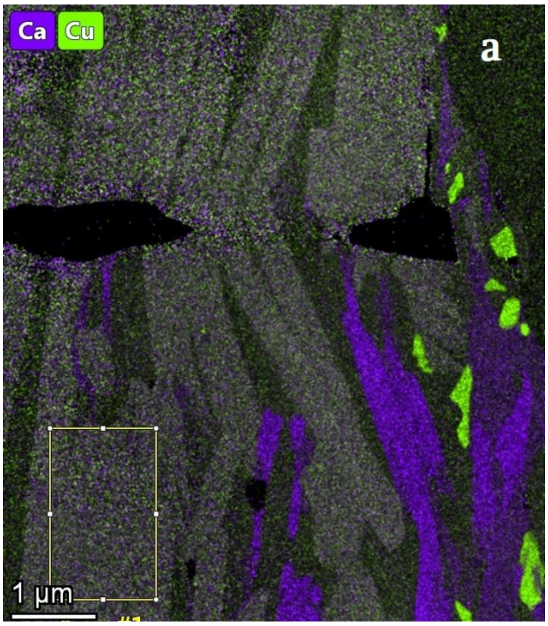

Fig. 5. The TEM image of Bi(Pb)-2223 sample. a: elemental mapping with Ca and Cu elements.

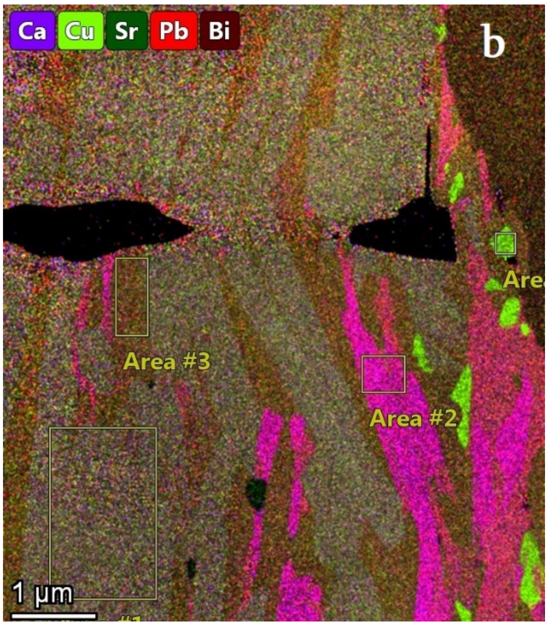

Fig. 6. The TEM image of Bi(Pb)-2223 sample. b: elemental mapping involving Ca, Cu, Sr, Pb, Bi elements.

The results of the elemental analysis of the 1, 2 and 3 areas are summarized in Tables 2, 3, 4.

Table 2. Elemental analysis for the area 1

2020-02-14 11:05:33 Analysis of spectrum: Spectra from Area #1								
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
8	O	K	60.75	4.89	20.70	1.15	2.42
20	Ca	K	8.44	1.29	7.20	1.02	0.17
29	Cu	K	13.72	2.11	18.57	2.64	0.06
38	Sr	K	8.71	1.30	16.27	2.24	0.37
82	Pb	L	1.23	0.17	5.41	0.67	0.32
83	Bi	L	7.15	0.98	31.85	3.95	0.17

Table 3. Elemental analysis for the area 2

2020-02-14 11:05:33 Analysis of spectrum: Spectra from Area #2							
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
8	O	K	57.73	5.61	18.19	1.21	2.85
20	Ca	K	23.15	3.76	18.28	2.67	0.14
29	Cu	K	2.89	0.47	3.61	0.53	0.74
38	Sr	K	2.71	0.43	4.68	0.67	1.66
82	Pb	L	11.51	1.69	46.98	6.03	0.31
83	Bi	L	2.01	0.29	8.25	1.06	0.86

Table 4. Elemental analysis for the area 3

2020-02-14 11:05:33 Analysis of spectrum: Spectra from Area #3							
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit Error (%)
8	O	K	57.40	5.13	14.99	0.91	0.26
20	Ca	K	4.77	0.76	3.12	0.46	0.45
29	Cu	K	10.89	1.75	11.30	1.65	0.51
38	Sr	K	10.73	1.68	15.35	2.18	0.48
82	Pb	L	2.22	0.32	7.51	0.97	0.80
83	Bi	L	13.99	2.02	47.72	6.13	0.24

Atomic fractions of elements for area 1 correspond fairly well to the chemical composition of Bi(Pb)-2223 superconductor.

Conclusions

Influence of B_4C–doping on structure, microstructure and phase evolution of Bi(Pb)-2223 have been investigated. Positive role of B_4C additive for Bi(Pb)-2223 phase formation was confirmed. Gradual decrease of lattice parameters with increasing doping level suggests the partial substitution of boron for copper. Completed solid-state reaction, non-reacted and poorly formed superconducting areas were revealed by the TEM/STEM analysis.

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ფიზიკა

B_4C-ით დოპირებული Bi(Pb)-2223 ზეგამტარის სტრუქტურული თავისებურების შესახებ

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** საქართველოს ტექნიკური უნივერსიტეტი, ვლადიმერ ჭავჭანიძის სახ. კიბერნეტიკის ინსტიტუტი, თბილისი, საქართველო*

(წარმოდგენილია აკადემიის წევრის ა. ხელაშვილის მიერ)

წარმოდგენილ ნაშრომში შესწავლილია ბორის კარბიდის (B_4C) დანამატის გავლენა Bi(Pb)-2223 მაღალტემპერატურული ზეგამტარი ფაზის ფორმირებასა და სტრუქტურულ თვისებებზე. $Bi_{1.7}Pb_{0.3}Sr_2Ca_2Cu_3O_y(B_4C)_x$, x=0, 0.040 და 0,075 ნომინალური შედგენილობის მქონე საყრდენი და B_4C-დანამატიანი Bi(Pb)-2223 ნიმუშები სინთეზირებულ იქნა მყარ-ფაზური რეაქციის მეთოდით. პრეკურსორი ფხვნილები ხელით დაიფქვა აქატის ჯამში და გამოიწვა 850^0C ტემპერატურაზე, 30 სთ განმავლობაში, შუალედური გადაფქვებით; მიღებული მასალები დაიწნეხა აბების სახით და გამოიწვა 845^0C ტემპერატურაზე, 40 სთ განმავლობაში. Bi(Pb)-2223 ფაზის ევოლუცია მიღებულ ნიმუშებში შესწავლილ იქნა რენტგენოდიფრაქციული ანალიზით და ანალიზის მონაცემების საფუძველზე შეფასდა Bi(Pb)-2223 ფაზის მოცულობითი წილი. რენტგენოგრამების გამოყენებით გამოთვლილ იქნა Bi(Pb)-2223 ფაზის მესრის პარამეტრები. კუთრი წინაღობის ტემპერატურული დამოკიდებულება გაიზომა ოთხკონტაქტიანი მეთოდით. ტრანსმისიური და მასკანირებელი ტრანსმისიური ელექტრონული მიკროსკოპიის მეთოდით ჩატარდა სინთეზირებული ნიმუშების მიკროსტრუქტურული და ელემენტური ანალიზი. კუთრი წინაღობის ტემპერატურულმა დამოკიდებულებებმა გამოავლინა ორსაფეხუროვანი ზეგამტარული გადასვლა კრიტიკული ტემპერატურით T_c>100K, რაც მიანიშნებს მაღალტემპერატურული 2223 და დაბალტემპერატურული 2212 ფაზების თანაარსებობაზე მიღებულ მასალებში. რენტგენოდიფრაქციულმა ანალიზმა დაადასტურა Bi(Pb)-2223 ფაზის მოცულობითი წილის საგრძნობი გაუმჯობესება 56%-დან არადოპირებული ნიმუშისათვის 88%-მდე, როცა x=0,04. მესრის პარამეტრების თანდათანობით შემცირება დოპირების დონის ზრდისას მიუთითებს Cu^{2+} იონების ნაწილობრივ ჩანაცვლებაზე B^{3+} იონებით. ტრანსმისიური და მასკანირებელი ტრანსმისიური ელექტრონული მიკროსკოპიისა და ელემენტური ანალიზის მეშვეობით ვიზუალურად გამოვლინდა სრულად ფორმირებული, ნაწილობრივ ფორმირებული და ჩამოუყალიბებელი Bi(Pb)-2223 ფაზის არეები.

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