THE EFFECT ON STRUCTURAL AND SURFACE MORPHOLOGICAL PROPERTIES OF NANOSTRUCTURED Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$BASED HIGH TEMPERATURE SUPERCONDUCTORS

InduVerma $^1$, Ritesh Kumar $^1$ and Nidhi Verma $^1$

$^1$ Departments of Physics, University of Lucknow, Lucknow-226007, India
E-mail: indunano@rediffmail.com

Abstract-
The effects of Surface morphological Properties of Nanostructured Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ based High Temperature Superconductors have been investigated. Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ superconducting samples are prepared by solid-state reaction route. Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ superconductors were prepared in bulk form. The phase identification /gross structural characteristics of synthesized (HTSC) materials explored through powder x-ray diffractometer reveals that all the samples crystallize in orthorhombic structure with lattice parameters $a = 5.4918\,\text{Å}$, $b = 5.4071\,\text{Å}$ and $c = 37.0608\,\text{Å}$. The critical temperature ($T_c$) measured by standard four probe method has been found to be 108 K. The surface morphology investigated through scanning electron microscope and atomic force microscopy (SEM & AFM) results that small voids & larger grains size besides, nanosphere like structures on the surface of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ sample.

Keywords: Bi-2223, SEM AFM and HTSC.

I. INTRODUCTION

The Bi-2223 phase seems to dominate in all the three system in spite of the fact that single-phase formation is very difficult. However it has been reported [1-3] that the addition of Pb at Bi-sites promotes the formation of single 2223 phase. Several studies of elemental substitution at different sites (cations) and their effects on structural and superconducting properties of the compound (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{y}$ have been reported in the literature [4-5]. The relation between the suppression of the superconductivity and the local magnetic moment of impurities by the partial replacement/doping of cations or anions with other element has generated a great deal of interest in high temperature superconductors. It is also a powerful tool to obtain useful information on the crystal structure and to establish general phenomenological trends that provide a better insight into the factor that give rise to high $T_c$ in high temperature superconductors. Zn substitution is nonmagnetic and does not lead to these phenomena [6].

Nkum et.al. [7] have investigated the Vanadium substitution at Cu site of (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ (Bi-2223) samples by means of X-ray diffraction and electrical resistivity measurements [8-16]. The volume fraction of the V substituted Bi- 2223 phase decreases with a decrease in the c- lattice parameter. The critical temperature $T_{c_{onset}}$ of the samples remains almost constant while the temperature at which the resistance becomes zero decreases with increasing dopant content [17-20]. The electrical resistivity data suggest that the substitution of copper by vanadium.
suppresses the superconductivity in (Bi,Pb)$_2$Sr$_2$Ca$_2$Cu$_{3-x}$V$_x$O$_y$ by destroying the phase coherence and by pair-breaking effects. The suppression of superconductivity in the system could also be due to a decrease in the carrier concentration [21, 22].

II. EXPERIMENTAL DETAILS

The sample Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ was prepared by standard solid-state reaction method accompanied by three stage calcinations processes in air at temperatures 800°C for 18 hrs, 820°C for 20 hrs and 840°C for 24 hrs with a heating rate of 3°C/min. In brief, the powders of high grade purity Bi$_2$O$_3$ (99.99%, Alfa Aesar), PbO (99.99%, Alfa Aesar), SrCO$_3$ (99.9%, Alfa Aesar), CaCO$_3$ (99.9%, Alfa Aesar), CuO (99.99%, Alfa Aesar) and ZnO (99.99%, Alfa Aesar) were mixed and ground in an agate mortar pestle, put in cylindrical boats and calcined at 810°C for 24 hrs in air. After calcinations the as synthesized powder were pelletized using a rectangular die of 2mm×4mm under a force of 300-400 kg/cm$^2$. Pressed pellets were partially melt textured at 848°C (very near to melting) for 40 hrs. The gross structure and phase analysis of the samples at different stages of calcinations were carried out by powder X-ray diffractometer (18KW rotating anode Cu target, Rigaku, Japan). The surface morphology of the as partially melted pellets were carried out through Joel scanning electron microscopy (SEM, JSM-5600) and Nanoscope-E digital Instruments atomic force microscopy (AFM). From the AFM analysis, the uniform crystallinity, surface homogeneity, and nanocrystal grain nature is clearly identified for the melt textured samples prepared in the present work. Also the AFM was used to measure the roughness (R) of the samples.

III. RESULTS AND DISCUSSION

Fig. 1 shows the representative X-ray powder diffraction pattern for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$. Besides Bi-2223 as major phase, some other minority phases indexed by starred (*) sign were also found. The crystal structure of Bi-2223 is found to be orthorhombic with a = 5.4048 Å, b = 5.4358 Å and c = 37.0634 Å for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ sample. The presence of impurity phases is significant in other Zn substituted Bi-2223 samples of higher Zn-concentration, which are Zn-rich compounds due to the easier formation of Zn–Cu clusters. These starred peaks were identified as CaZnO$_2$, CuZnO$_2$, and unreacted ZnO. These Zn-rich compounds reduce the amount of Bi-2223 phase and enhance the formation of Bi-2212 phase.

![XRD of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ sample.](image1)

Fig. 1 XRD of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ sample.

Fig. 2 shows the SEM image of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ sample revealed the small in grain and large porosity size. The pores / voids between the grains also increase with Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+x}$ sample. For
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![Image](image1.jpg)

**Fig. 2 SEM of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ sample.**

Figure 3 shows the 2D image appears as nanogranules of different shapes in which some sites are predominantly oxidized over others. In order to check the difference in thickness profiles, line scans were also carried out across the oxides scales formed on the both phases. The most pronounced difference in the two layers of oxide is around 10 to 100 nm.

![Image](image2.jpg)

**Figure 3** shows the 2D image appears as nanogranules of different shapes in which some sites are predominantly oxidized over others. In order to check the difference in thickness profiles, line scans were also carried out across the oxides scales formed on the both phases. The most pronounced difference in the two layers of oxide is around 10 to 100 nm.

Figure 4 shows the 3D AFM image of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ sample are again showing nanogranules like structures on the surface. In the three dimensional (3D) AFM view of the same surface the formation of the humps & roughness in some places could also be clearly seen, which is due to formation of oxide layer with different thickness depending on the chemical composition of phases. Besides the said features, two types of inhomogeneities have been observed in our investigations. The inhomogeneities of the first type are planar nanogranules and the inhomogeneities of the second type are closely packed planar rounded nanogranules forming a scaly surface. Surface roughness is calculated as the standard deviation of the mean height of surface structures as shown in figure 4. The value of roughness is found to be 170.6 nm.
IV. CONCLUSIONS

The sample Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ were prepared by standard solid-state reaction method. The crystal structure of Bi-2223 is found to be orthorhombic with $a = 5.4048$ Å, $b = 5.4358$ Å and $c = 37.0634$ Å for Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ sample. Fig. 2 shows the SEM image of Zn doped Bi-2223 clearly revealed the smaller grain size and larger porosity. The compact granular structure of various shaped thin grains and larger pores are observed in some local region. The 2D AFM image of Bi$_{1.6}$Pb$_{0.4}$Sr$_2$Ca$_2$Cu$_{2.70}$Zn$_{0.30}$O$_{10+\delta}$ sample revealed the nanogranular structure on the surface. In the three dimensional (3D) AFM view of the same surface the formation of the humps & roughness in some places could also be clearly seen, which is due to formation of oxide layer with different thickness depending on the chemical composition of phases. Surface roughness is calculated as the standard deviation of the mean height of surface structures as shown in figure 4. The value of roughness is found to be 170.6 nm.

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