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EDAX MICROANALYSIS OF Sn DOPED (Bi,Pb)-2223 IN Ca SITE: A POTENTIAL METHOD IN DETERIMINING SUPERCONDUCTING PHASE

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ABSTRACT. A series of $Bi_{1.7}Pb_{0.3}Sr_2(Ca_{1-x}Sn_x)_2Cu_3O_{10-\delta}$ superconducting ceramics with tin concentration of x = 0 – 0.1 were synthesized using the solid state method. The samples were then characterised to determine the critical temperature (T_c) by conducting the resistivity experiment; determination of dominant superconducting phase using the SEM and EDAX; and calculation of the volume fraction of the superconducting phases using XRD. Resistivity measurements showed that the T_c dropped from 105K to 45K as Sn concentration increased from 0 to 0.1 indicating superconducting phase change from the 2223 high-T_c to the 2212 low-T_c phase. SEM micrographs showed a significant change from porous plate-like to more rectangular granular grains. Further EDAX microanalysis quantified the compositional changes and calculation of the Ca:Cu ratio showed a reduction from 9.8% to 32%, indication of dominant phase change from 2223 phase with volume fraction of 97% – 30 % to the 2212 phase with volume fraction of 15% – 75%.

KEYWORDS. BSCCO system, volume fraction, 2223 high-T_c phase, 2212 low-T_c phase

INTRODUCTION

It is well known that the Pb modified $Bi_2Sr_2Ca_2Cu_3O_8$ (BSCCO) assists the formation of the high-T_c phase in the system, (Maeda *et al.*, 1988). Many substitutional studies have been made in the BSCCO system as it offers a wide range of isomorphic replacements according to Thamizhavel *et al.* 1997, Halim *et al.* (1999) and Smrckova *et al.* (1998). The substitution in the charge reservoir layer affects the amount of charge on the conduction planes, thereby causing an increase or decrease in the transition temperature (T_c) and creates structural defects which affect the transport properties (Retoux *et al.*, 1989).

There are three principal phases in the system having a general formula of $Bi,Pb_2Sr_2Ca_{n-1}Cu_nO_{2n+4}$ namely the 2201, 2212 and 2223 phase with T_c of 10K, 90K and 110K for n = 1, 2 and 3 respectively according to Bernik *et al.* (1994). The BSCCO system is a complex structure that has created various interests in the surface morphological and structural studies of phases formed in the material. The structural characterisation of these oxides has been carried out by using x-ray diffraction, (Halim *et al.*, 1999), neutron diffraction, (Kajitani *et al.*, 1988), TEM and electron diffraction, (Tendeloo & Krekels, 2000), SEM and energy dispersive x-ray spectrometry (EDAX) techniques (Zulkifli *et al.* 1999).

In the field of superconducting ceramics, the use of electron microscopy accompanied by energy dispersive spectroscopy not only can determine the composition and structures of the material, it also can be a tool to give an estimation of the dominant superconducting phase, in which the phase is characterised by the T_c value as stated by Bernik *et al.* (1994) and Tendeloo & Krekels (2000). From the EDAX quantitative analysis, the most important feature of the spectrum derived are the Cu and Ca peaks whereby these peaks influenced the microstructural change especially in determining the superconducting phases of 2212 or 2223 phase.

MATERIAL AND METHOD

The ceramic samples of $Bi_2Pb_{0.6}Sr_2Ca_{2-x}Sn_xCu_3O_\delta$ ($x = 0.00 - 0.1$) were prepared by solid state method using high purity (<99.9%) of Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, SnO_2, and CuO powders according to its stoichiometric ratio. The electrical resistance was measured with temperature range of 20 – 300K by a standard four point probe technique using samples maintained in a Leybold's helium closed cycle cryogenic system. The phase identifications was carried out by using the XRD with copper K_α radiation.

The microstructural characterisation was done using the SEM model Philips XL30, using accelerator voltage of 15kV at magnifications of 500x and 2000x. Microanalysis was performed for both magnification to gather general and detailed chemical compositional analyses using the attached EDAX with its integrated EDAX analyser (DX4i) and control software.

RESULTS AND DISCUSSION

The normalised resistance vs. temperature curves for the tin doped samples for $x = 0 - 0.1$ is shown in Figure 1. All samples exhibit $T_{c\ onset}$ around 110K. The curves showed a transition from $T_{c0} > 100K$ to 60K, indicated a shift from 2223 to 2212 phase as x increased. Derivation of resistance with temperature in Figure 2 clearly revealed the shift towards lower superconducting phase when tin is increased.

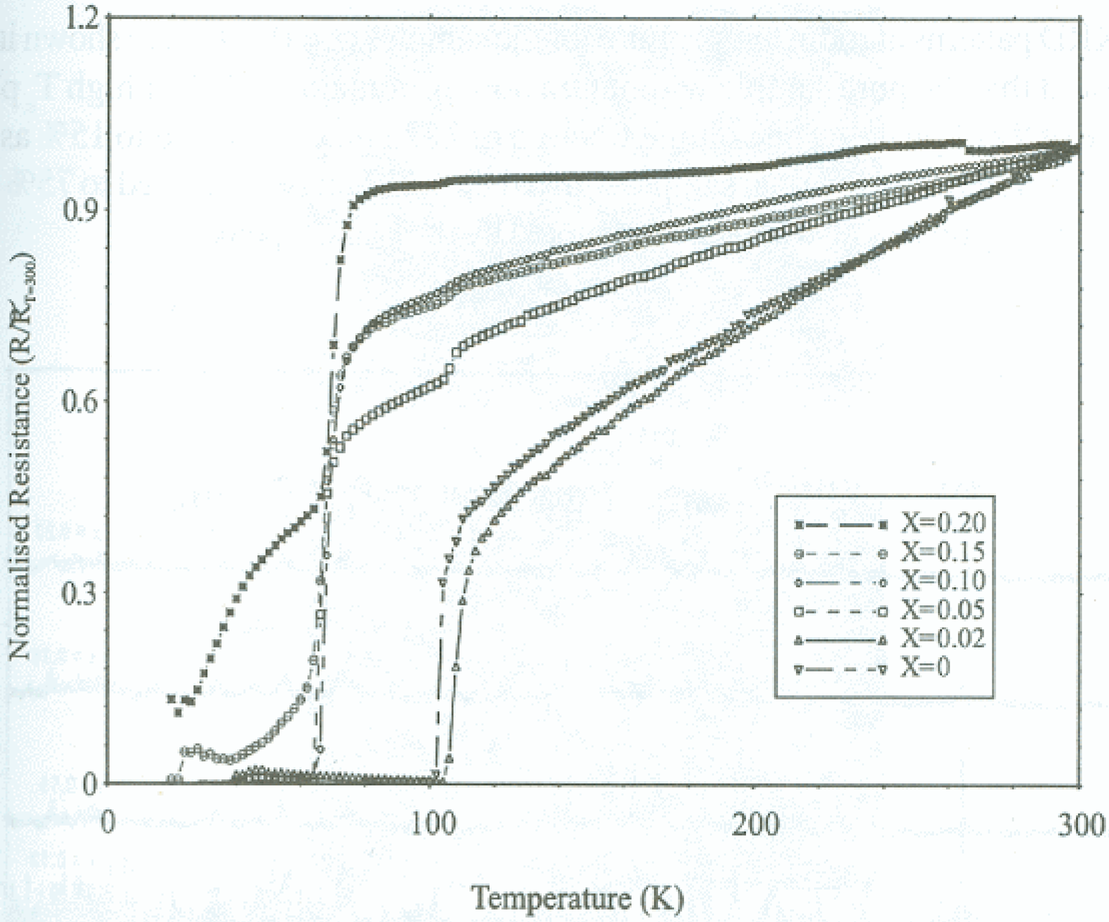

Figure 1. Normalised Resistance vs. Temperature Graph for Sn Doped BSCCO

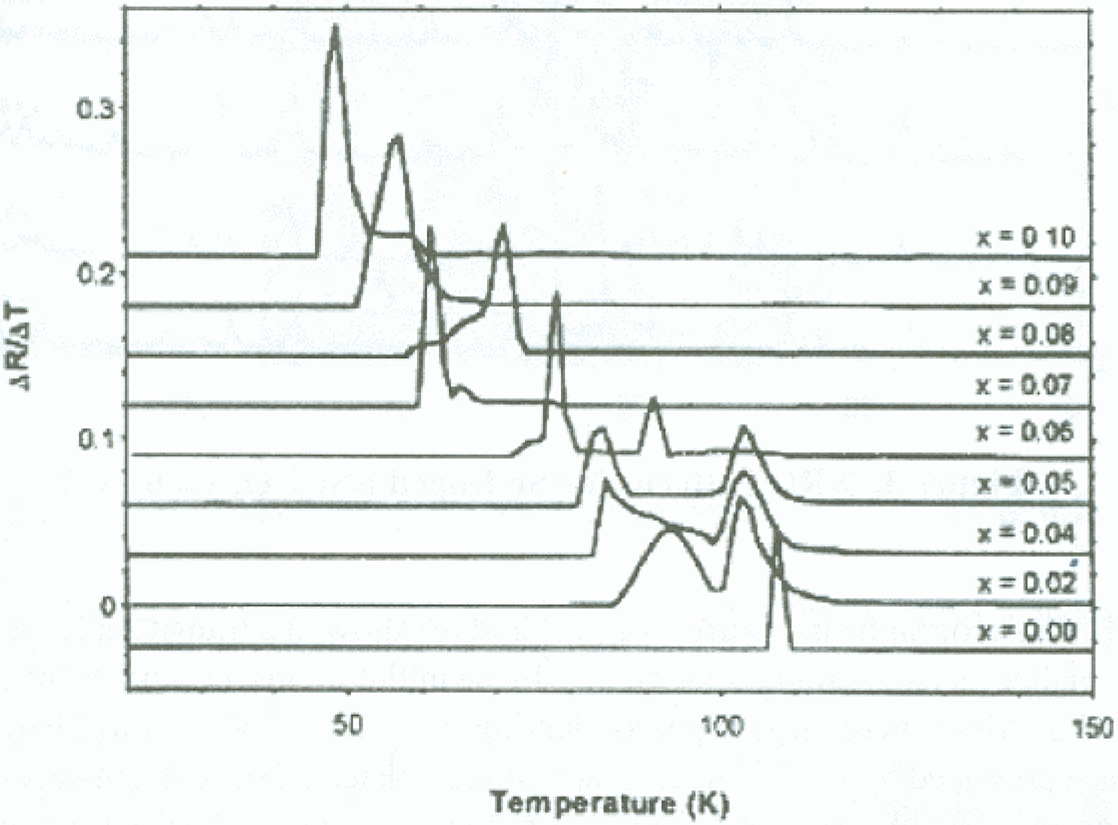

Figure 2. Derivation of resistance vs. temperature for Sn Doped BSCCO

The XRD patterns at room temperature for the samples (x = 0 – 0.2) are shown in Figure 3. It also showed that the pure sample without tin doping contained 98% of high T_c phase (H peaks) and 2% of 2212 phase. The volume fraction of 2223 phase reduced to 15% as tin was introduced in the system and the final sample showed the 2212 phase increased to 75% as other non-superconducting phases also appeared, denoted by the L and * peaks.

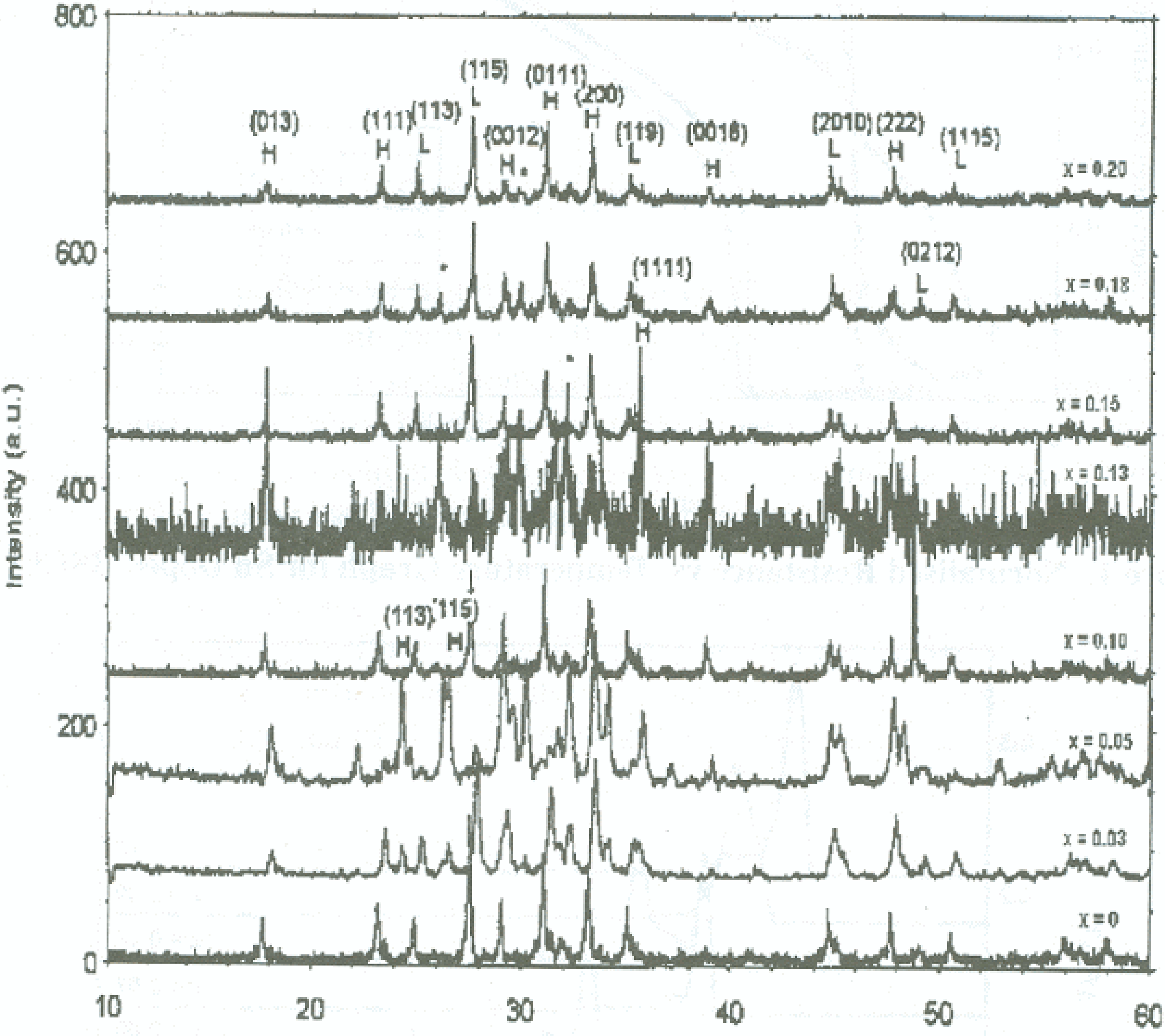

Figure 3. XRD Patterns for Sn Doped BSCCO, x = 0 – 0.2

SEM micrographs in Figure 4 (a), (b) and (c) showed a transition from large flaky grains to smaller rectangular granular grains. In the initial sample (x = 0), the microstructure showed the distribution of large superconducting flaky-like structures while the transition samples as represented by x = 0.05 micrograph, some isolated clusters of non-superconducting granular grains were observed and the flakes reduced in size. In the final sample (x = 0.1), the flakes were very fine and the rectangular grains increased randomly oriented with larger voids within the matrix.

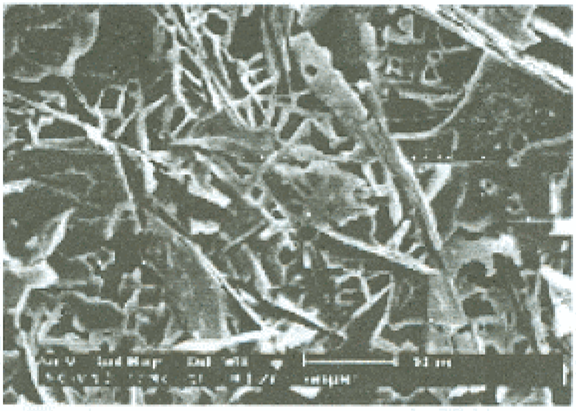

Figure 4 (a): x = 0

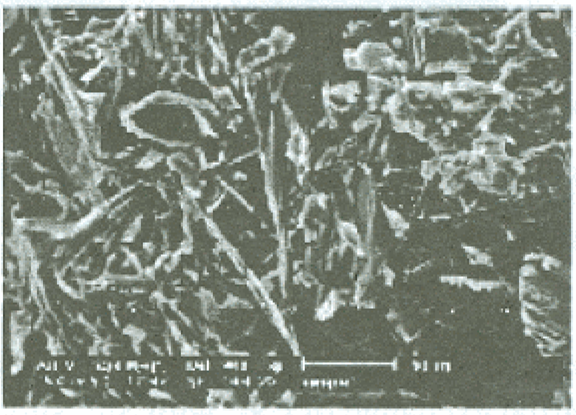

Figure 4 (b): x = 0.1

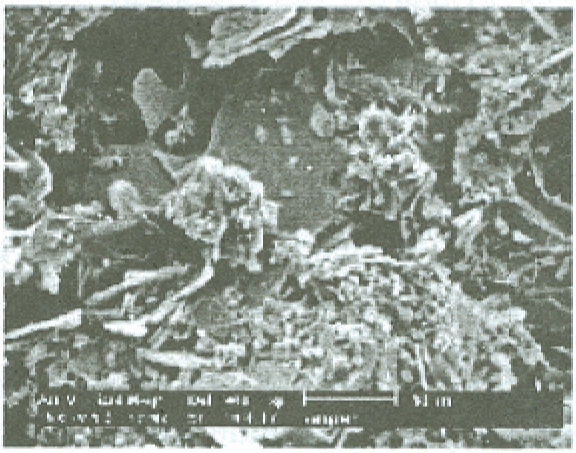

Figure 4 (c): x = 0.2

Figure 4. (a-c) Micrograph of Sn doped BSCCO, x = 0, 0.1 & 0.2

EDAX microanalyses showed that there was a reduction for both Ca and Cu atoms, as shown both in Figure 5. As the doping of Sn increased, the concentration of Ca and Cu is reduced, indicted that the phases converted from the high-Tc 2223 phase to the low-Tc 2212 phase. Atomic ratios of elements were normalised to Cu = 3 and the concentration of Bi obtained by the standardless ZAF method is always too high regardless of the overall concentration. On the other hand, the results obtained for other elements by the standardless method for superconducting and non-superconducting phases were comparable.

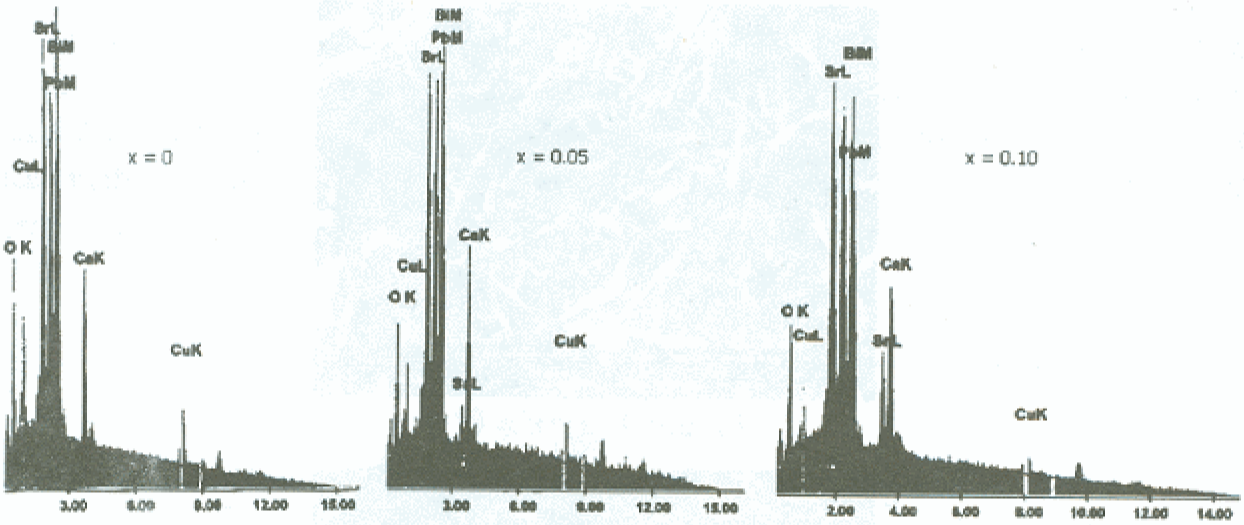

Figure 5. EDAX Spectrums of Sn Doped BSCCO,x = 0, 0.1 & 0.2

CONCLUSION

BSCCO system with tin doping, x = 0.00 – 0.1 superconducting ceramics were successfully made. The partial exchange of Ca^{2+} with Sn^{2+} suppressed the T_c from 100K to 60K. Findings from this research showed that the EDAX microanalysis through its standardless analysis enables a quick and convenient method to determine the superconducting and secondary phases in the BSCCO system. The Ca and Cu peaks in the spectra of the high T_c phase obviously differed when normalised on Bi, which enabled quick and convenient identification of the 2223 or 2212 phase.

From the microanalysis, it is shown that the texture of the morphology of samples play an important role to deterime the transport property of the samples. As the substitution process is being done, a complex composition is developed. This compound is prone to exposed to structural defects such as layered defects, anti-site defect and the formation of impurities especially in the CuO_2 planes. In addition to that, as the oxygenation process is done during heating and annealing, the compound might go through an oxygen stoichiometric change causing oxygen deficient which in turn affects the pinning intensity and the T_c value. Another contribution to T_c change is the change in the ionic radius and valency of Sn^{2+} and Ca^{2+}. It causes distortion and defects within the crystal as well as affects the formation of Cooper pairs responsible for the supercurrent for the material in the CuO_2 planes.

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