STUDY OF ELECTRICAL TRANSPORT PROPERTY OF

$YBa_2Cu_3O_{7-\delta}$ + x $BaSnO_3$ SUPERCONDUCTOR

A REPORT SUBMITTED

TO

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BY

Debasish Giri

M.Sc PHYSICS

ROLL NO : 411PH2093

UNDER THE SUPERVISION OF

Prof. D. Behera

Department of physics, NIT Rourkela

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

CERTIFICATE

This is to certify that the thesis entitled **" Study of Electrical transport property of YBCO+ x BSO Superconductor "** submitted by Debasish Giri in partial fulfilments for the requirement for the award of master of science degree on physics department at National Institute of Technology, Rourkela is an reliable work carried out by him under my supervision and direction. To the best of my knowledge, the matter embodied in the project has not been submitted to any other University/Institute for the award of any degree.

Prof. D. Behera

Department of Physics

NIT, Rourkela

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Rourkela

Date

Debasish Giri

ABSTRACT

Pristine $YBa_2Cu_3O_{7-\delta}$ (YBCO) and dielectric $BaSnO_3$ samples are prepared by solid state route. BSO is used as composite materials because of its advantages properties. The samples are characterised by SEM to study the grain morphology and also characterised by R ~ T measurement performed by four probe method. . From the R-T plot it is observed that T_c value increases with the increase in BSO wt.% in the composites which affects the electrical transport property. T_c value increases upto 2.5 wt.%. Beyond 2.5 wt.% the graphs shows no transition. The normal state resistivity at 300K increases with BSO addition. Decreasing value of ΔT_c signifies that BSO addition affects the intergranular weak links.There in no change in grain size with the addition of BSO.

CONTENT

CHAPTER- I

1. INTRODUCTION

1.1 General remarks

Superconductivity was discovered by Dutch Physicist Heike Kamerlingh Onnes in 1911 while working at low temperature. Superconductivity is the property of metal, alloys, and chemical compound at temperature called transition temperature or critical temperature where electrical resistivity vanishes and they becomes diamagnetic in nature due to Meissner effect. Superconductors are extraordinary because resistance is zero so it devoid of Jule's heating. The conductivity is infinity with no loss of energy. A dramatic variation in the research activity has taken place when high temperature superconductors (HTSC) having T_c of 90 K, above the boiling point of liquid nitrogen (77 K), was discovered in $YBa_2Cu_3O_{7-\delta}$ (YBCO) in the year 1986. The operating device with zero-resistance at liquid-nitrogen temperature has fuelled worldwide interest for power applications like superconducting magnets, motors and power-transmission lines etc. In the field of electronics, extensive studies on Josephson junction, Josephson computers and the progress of commercial superconducting quantum interference device (SQUID) systems are now applied for characterization of materials.

Properties of superconductors

Most of the physical properties of superconductors vary from material to material, for example the heat capacity and the critical temperature, critical current density, and critical field at which superconductivity is destroyed. For instance, all superconductors have exactly zero resistivity to low applied currents when there is no magnetic field present or if the applied field does not exceed a critical value.

- **Zero electrical resistance :**

Some materials are placed in series with a current source I and measure the resulting voltage V across the sample. The resistance of the specimen is given by Ohm's law $R=V/I$. If the voltage is zero, this means that the resistance is zero and that the sample is in the superconducting state. Superconductors are also able to sustain a current with no applied voltage.

- **Superconductors obey Meissners effect :**

A superconductor with little or no magnetic field within it is said to be in the Meissner state. Meissner and ochsenfeld measured flux distribution outside tin and lead specimens which has been cooled below their transition temperature while in a magnetic field. They set up their transition temperatures the specimens spontaneously became perfectly diamagnetic. Superconductor not ever has a flux density even when in applied magnetic field (B=0).

- **Effect of magnetic field :**

The superconducting state of a metal exist only in a particular range of temperature and field strength. Superconducting state appear in the metal is that some combination of temperature and field strength should be less then critical value. It will disappear if the temperature of the specimen is raised above its Tc or sufficiently strong magnetic field is employed.

$$H_c = H_o [1- (T/T_c)^2] \quad \text{Where,}$$

H_c - Extreme critical field strength at the temperature T.

H_o - Extreme critical field strength occurring at absolute zero

T_c - Critical temperature the highest temperature of superconductivity.

- **Effect of current :**

The magnetic field that causes a superconductor to become normal from a superconducting state is not necessarily by an external applied field. It may arise as a result of electric current flow in the conductor. The least current that can be passed in a sample without disturbing its superconductivity, that is called critical current I_c. If a wire of radius ‘r’ of a type-1 superconductor carries a current ‘I’, there is a surface magnetic field, $H_i = I/2\pi r$, associated with the current. If H_i beats H_c, the materials go normal. If in addition a transverse magnetic field ‘H’ is applied to the wire, the condition for the switch to the normal state at the surface is that the sum of the applied field and the field due to the current should be equal to the critical field.

$$H_c = H_i+2H$$

This is called Silsbee’s rule. The critical current I_c will decrease linearly with increase of applied field until it reaches zero at $H = H_c/2$. If the applied field is zero $I_c = 2\pi rH_c$.

- **Penetration depth :**

F.London and H.London described the meissner effect and zero resistivity by adding the two condition E= 0 (from the absence of resistivity) and B= 0 (from meissners effect) to Maxwell electromagnetic equation. According to that the applied field does not suddenly drop to zero at the surface of the superconductor, then decays exponentially according to the equation,

$$H = H_0 \exp(-x/\lambda)$$

Where

H_0 - value of magnetic field at the surface

λ - penetration depth; λ is the distance for H to fall from Ho to Ho/e.

Types of superconductors

(I) Type - I superconductors (Low T_c superconductors)

(II) Type - II superconductors (High T_c superconductor)

1.2 Type-I superconductor :

All the elemental superconductors exhibit flux expulsion (Meissner effect) up to a critical magnetic field (H_c) beyond which flux penetrates the material and drives it to normal state. This type of superconductors are called type-I superconductor. Very pure samples of Pb, Hg and Sn are examples of Type-I superconductors. Type-I superconductors are also known as soft superconductors as they can not bear high magnetic field. With small field they are turned to normal materials.

1.3 Type-II superconductors :

Type-II superconductors are also known as hard superconductors due to bearing of high magnetic field. High temperature ceramic cuprate superconductors for example YBCO, BSCCO, TlBCCO, HBCCO are the examples of Type II superconductors. This type of superconductivity is showed by transition metals with high values of the electrical resistivity in the normal state that is the electronic mean free path in the normal state is short. The figure below shows the behavior of magnetic field to material. It obeys Meissner effect upto certain critical field H_{c1} at which magnetic flux begins to enter the superconductor and an upper critical field H_{c2} at which superconductivity disappears.

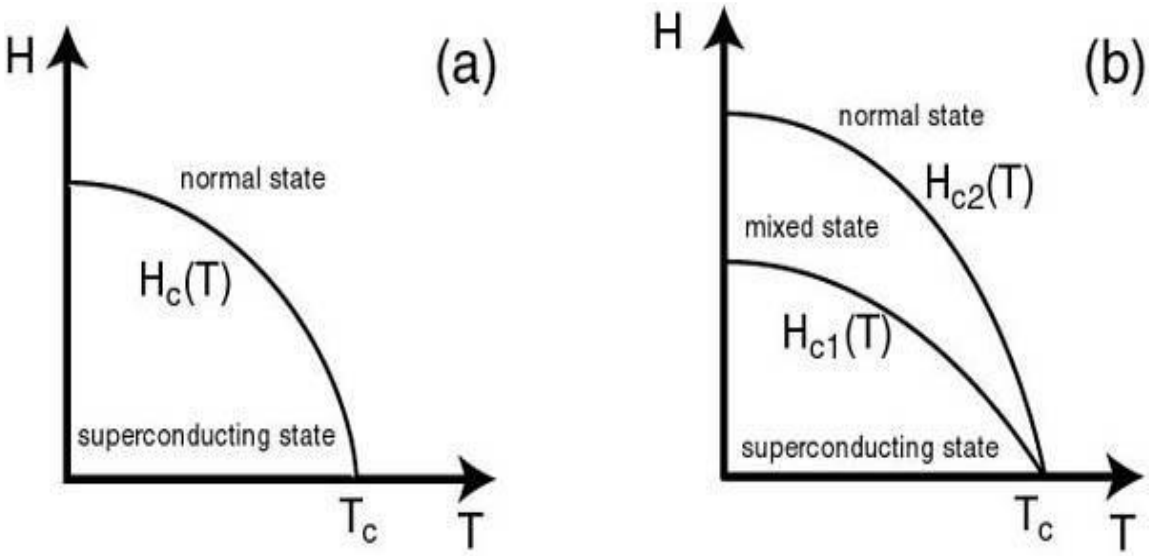

Fig.1: Magnetic phase diagram H (T) for (a) Type–I superconductor, one critical field Hc exists (b) Type-II superconductor, where two critical fields exist (Lower critical field (H_{c1}) & upper critical field (H_{c2})

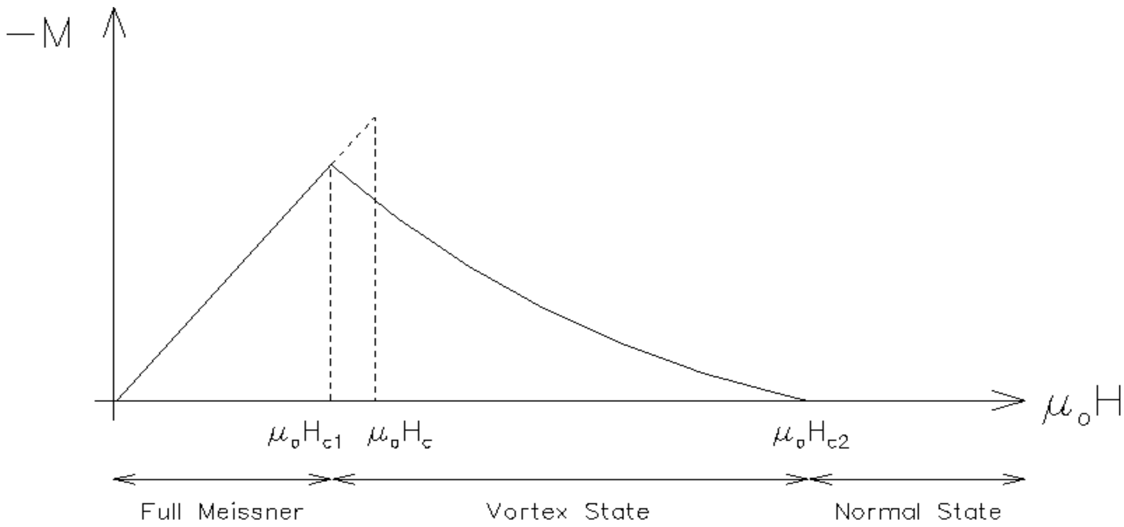

Fig.2: M – H graph showing the different state of a type-II superconductor

1.4 High -T_c superconductor :

Depending on transition temperature superconductors are also classified as low T_c and high T_c superconductors. Low T_c superconductors are mainly BCS superconductors. The superconductors above 30K are high T_c superconductors. The transition temperature obtained in the materials crosses the limit of BCS prediction. Hence, named as high temperature superconductor (HTSC). These materials are type II superconductors having large vortex state useful for large magnetic field applications.

$YBa_2Cu_3O_{7-\delta}$ HTSC

Yttrium barium copper oxide, often truncated as YBCO, is a crystalline chemical compound with the formula $YBa_2Cu_3O_{7-\delta}$. This was the first material to become superconducting beyond 77 K, the boiling point of liquid nitrogen. All materials developed earlier 1986 became superconducting only at temperatures near the boiling points of liquid helium or liquid hydrogen (Tb = 20.28 K) - the highest being Nb_3Ge at 23K. The significance of the discovery of YBCO is the much lower cost of the refrigerant used to cool the material to below the critical temperature.

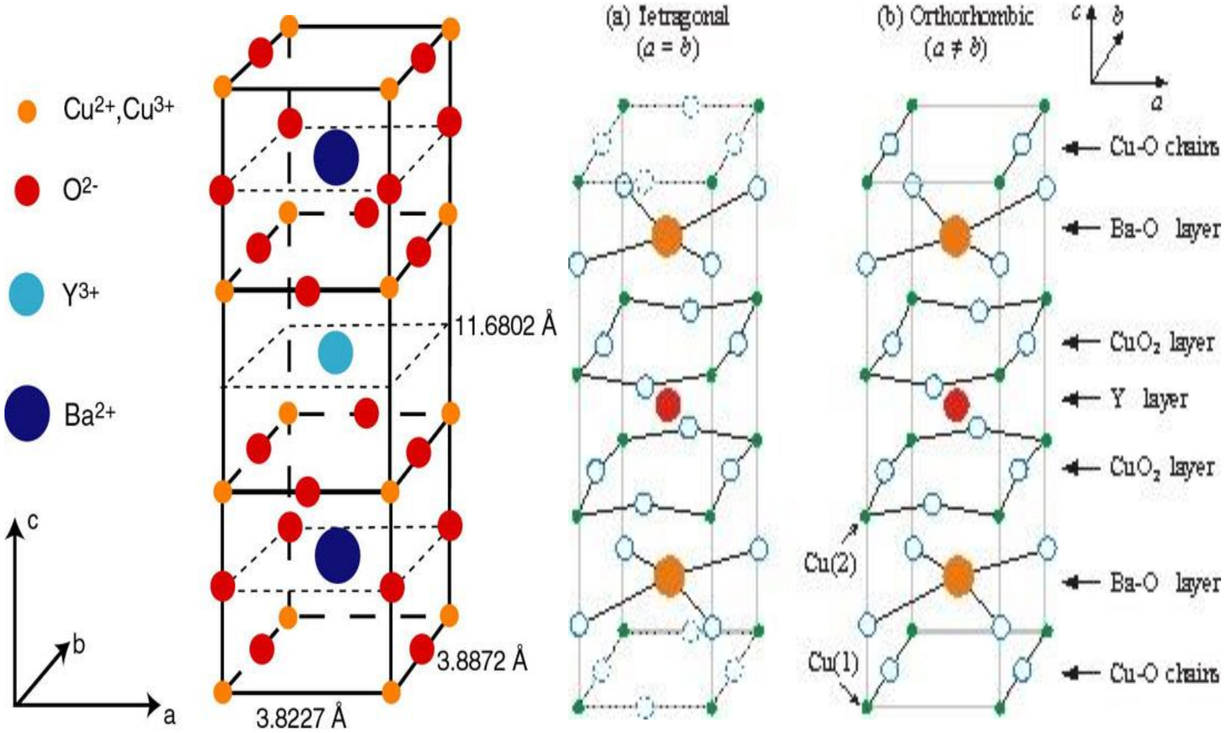

Fig.3: Structure of a single unit cell of YBCO. 3(a)Tetragonal and 3(b)Orthorhombic Structure of YBCO

The dimensions of a single unit cell of YBCO are a = 3.82 Å, b = 3.89 Å, and c = 11.68 Å. The lattice is composed of so-called perovskite layers ($ACuO_3$) where A is a rare-earth or alkaline-earth element (e.g.,Y or Ba in YBCO). The term 7-δ in the chemical formula implies a slight shortage of oxygen. If δ =0, the lattice is in the orthorhombic phase whereas in the circumstance of δ =1, the material has a tetragonal structure. Only the orthorhombic structure is superconducting but it is stable only at temperatures below 500°C.

1.5 Electronic - ceramic material $BaSnO_3$:

Barium stannate, $BaSnO_3$, belongs to the family of analogous alkaline-earth stannates (MSnO where M= Ca, Sr and Ba) which are currently being pursued for their attractive dielectric characteristics, finding application as thermally stable capacitors in electronic industries. In pure as well as in doped forms these stannates have also been investigated as potential sensor materials for a host of gases, including CO, HC, H_2, Cl_2, NO_x and humidity. There is great scope for exploiting heterojunctions of these stannates with other suitable oxides as capacitive sensors for carbon dioxide detection and metering . Recently, Ostrick et all have reported results of Hall measurements on BaSnO3 at high temperatures to eluci- date the nature of defects prevailing in the material. It has been reported that barium stannate has a band gap of 3.4 eV, which is well within the range of 3 – 3.5 eV, generally desired for gas sensor materials. By combining $BaTiO_3$ (BTO) with $BaSnO_3$ (BSO) multifunctional ceramic sensors can be developed which can detect temperature, relative humidity, and gases such as prozylene, acetylene and ethylene at ambient temperatures and pressures. Smith et all have prepared $BaSnO_3$ by solid-state method using stoichiometric amounts of $BaCO_3$ and SnO_2 and heating at 1200^0C for 16 h. The compound was then reground, pelletized and annealed in air at 1300^0C for 43 h. The compound was indexed as having a cubic perovskite structure with the lattice parameter a= 4.119 A^0.

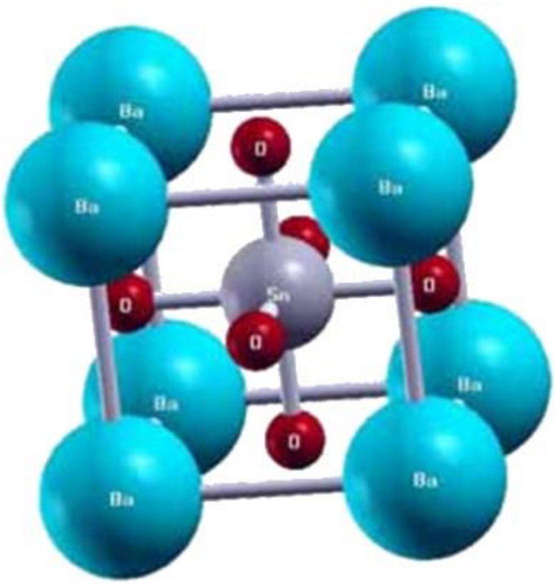

Fig.4: Primitive cubic structure of the $BaSnO_3$ perovskite material.

CHAPTER-II

2. Experimental Procedure:

$YBa_2Cu_3O_{7-\delta}$, $BaSnO_3$ were prepared separately by solid state rout method.

2.1 Preparation of $Yba_2Cu_3O_{7-\delta}$:

2. For the preparation of YBCO the precursor powders were in use as Y_2O_3, $BaCO_3$, CuO .

$$\frac{1}{2} Y_2O_3 + 2BaCO_3 + 3CuO + 1/2\ O_2 \rightarrow YBa_2Cu_3O_7 + 2CO_2$$

2. The above powder were mixed and ground well with Aget-moter and pestel for 2-3 hours resulting in gray powder.

3. This grounded powder was mixed with 2-methyle ethanol and stirred well for 12 hours.

4. This solution was dried and evaporated at 70-80^{o}c until well mixed powder were obtained.
5.Then the powder were calcinated at 900^{o}c for 15 hours in air to have crystallized $YBa_2Cu_3O_7$ powder followed by slow cooling to room temperature.

6. Regrinding the calcinated black solid for 2-3 hours.

2.2 Preparation of $BaSnO_3$

For the preparation of BSO the precursor powders were taken as $BaCO_3$ (barium carbonate) and SnO_2 (Tin Oxide).

$$BaCO_3 + SnO_2 \rightarrow BaSnO_3 + CO_2$$

1. The precursor powders were taken in the required proportions and ground and reground for 2- 4 hours.

2. Then the powder was calcined at 1200 ^{o}c for 16 hours to obtain $BaSnO_3$ powder.

CHAPTER-III

3. CHARACTERIZATION TECHNIQUES

3.1 Scanning electron microscope (SEM):

SEM stands for Scanning Electron Microscope. It is a microscope that uses electrons rather than light to form an image and to examine objects on a very fine scale. This examination can produce the following information:

Topography – surface features
Morphology – shape and size
Composition – elements and compounds/ relative amount of them

SEM is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons. The types of signals produced by an SEM include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode luminescence) sample current and transmitted electrons. Secondary electron detectors is common in all SEMs, but it is exceptional that a single machine would have detectors for all possible signals. The signals product from interactions of the electron beam with atoms at or near the surface of the sample. SEM Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are frequently used in analytical SEM along with the spectra made from the characteristic X-rays. Because the intensity of BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can deliver information about the distribution of different elements in the sample can produce very high-resolution images of a specimen surface, revealing details about less than 1 to 5 nm in size. Due to the very fine electron beam, SEM micrographs have a huge depth of field yielding a characteristic three-dimensional appearance useful for understanding the surface structure of a sample. Characteristic X-rays are emitted when the electron beam removes an inner shell electron from the specimen, causing a higher energy electron to fill the shell and discharge energy. These characteristic X-rays are used to identify the composition and measure the abundance of elements in the sample.

SEM components:

Electron Gun: Tungsten Filament

Lens System: Condenser and Objective Lenses

Detection System: electron/x-ray collector

Visual and recording cathode ray tubes (CRTs) and the electronics associated with them or computer

Filament: source of electron stream by thermionic or field emission. Cathode (negative electrode)

Grid Cap: is maintained at a negative potential. It is usually set at a voltage slightly more negative than the filament to provide a focusing effect on the beam.

Anode: is positive and attracts/accelerates the electrons down the column towards the lenses

Accelerating Voltage: voltage difference between the filament an the anode. At 20KV the filament will be placed at –20,000 V with respect to the anode,which is at grounded potential

Electromagnetic Lenses: are used to demagnify the diameter of the electron beam from 10-50 μm to a final spot size on the specimen (1 nm –1 μm). A magnetic field created by a current into a coil of N turns (cylindrical lens). Non-axial e-s experience unequal radial forces that make them spiral down the axis.

Important terms

• **Filament heating current**

The current used to resistively heat a thermionic filament to the temperature at which it emits electrons.

• Emission current

The flow of electrons which is emitted from the filament.

• Beam current

The portion of the electron current which goes through the hole in the anode.

• Electron Column

It consists of an electron gun and two or more electron lenses, operating in a vacuum.

• Electron Gun

It produces a source of electrons and accelerates these electrons to an energy in the range of 1- 40 keV. The beam diameter produced directly by the conventional electron gun is too large to generate a sharp image at high magnification.

• Electron lenses

These are used to reduce the diameter of this source of electrons and place a small, focused electron beam on the specimen. Most SEMs can generate an electron beam at the specimen surface with a spot size of less than 10 nm while still carrying sufficient current to form an acceptable image.

Working Distance (WD)

The distance between the objective lens and the surface of the specimen is called the working distance.

• Secondary Electron

These are electrons of the specimen ejected during inelastic scattering of the energetic beam electrons. The secondary electrons are defined purely on the basis of their kinetic energy; ie, all electrons emitted from the specimen with an energy less than 50 eV.

3.2 R-T Measurement by four probe method

The Four Probe Method is one of the standard and most widely used method for the measurement of resistivity. Four probe method is an electrical impedance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than traditional two-terminal (2T) sensing. The four probes are collinear and equally spaced. This error is due to contact resistance. That is especially serious in the electrical measurement, which can be avoided by the use of two extra contacts (probes) between the current contacts. For which in this arrangement the contact resistance may all be high compare to the specimen resistance, but as long as the resistance of the sample and contact resistances are small compared with the effective resistance of the voltage measuring device (potentiometer, electrometer or electronic voltmeter), the measured value remain unaffected. Because of the pressure contacts, this arrangement is also especially useful for quick measurement on different samples or sampling different parts of the same sample. The voltage drop is measured between the two probes labelled by means of a digital voltmeter. The potential drop across the contact resistance associated with probes is minimized, only the resistance associated with the superconductor between probes is measured. 4T sensing is used in some ohmmeters and impedance analyzers, in precision wiring configurations for strain gauges and resistance thermometers. The 4-point probes are also used to measure sheet resistance of specimen pellet.

CHAPTER-IV

4. RESULTS AND DISCUSSION:

4.1 Temperature dependent Resistivity Measurement:

Measurement of the resistivity dependence of temperature for different samples with various amounts of YBCO+xBSO and pure YBCO are shown in Fig.5 below. It is observed that Tc is affected due to addition BSO in YBCO. All samples show metallic behaviour in the normal state and as superconducting transition to zero resistance. At higher temperature, all samples exhibited linear temperature dependence. The resistive transition exhibits two different regions. The first is characterized by the normal state that shows a metallic behaviour (above 2Tc). The normal resistivity is found to be linear from room temperature to a certain temperature (100 K–300 K). The second is the region characterized by the contribution of Cooper pairs fluctuation to the conductivity below T_c, where $\rho(T)$ is deviating from linearity. This is mostly due to the increasing rate of cooper pair formation on decreasing the temperature.

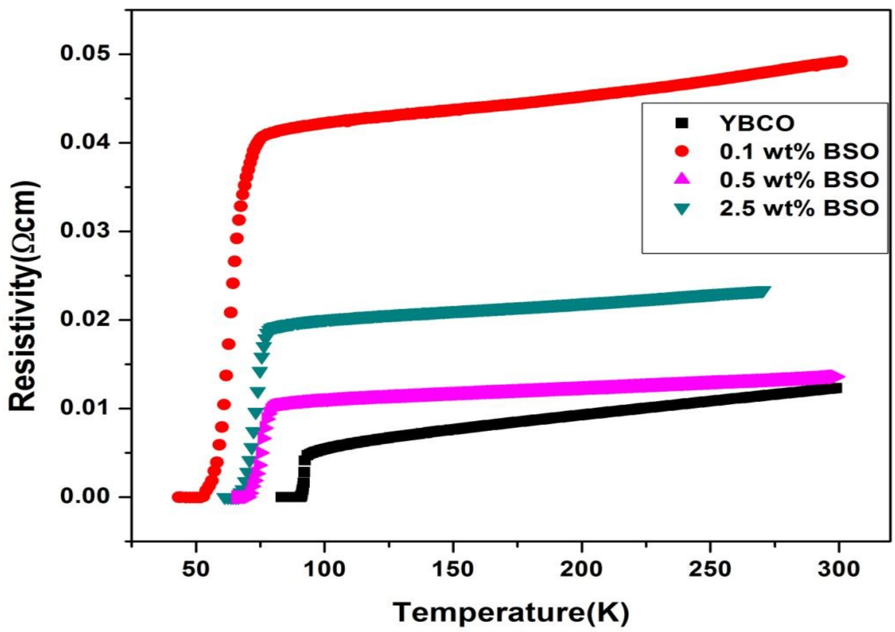

Fig 5. Temperature dependence of the resistivity for YBCO + x BSO(x = 0.0, 0.1,0.5, 2.5 wt.%) composites.

Differerent critical temperatures are observed from the different composites. The temperature derivative the resistivity curves are shown in fig.6 below. Tc is defined as the peak position of the derivative and is observed to increases with increasing wt. % of BSO. The peak broadening is occurring due to addition of BSO composite.The peak broadening decreases with increase in wt. % of BSO, which is affecting the intergranular link between grains.

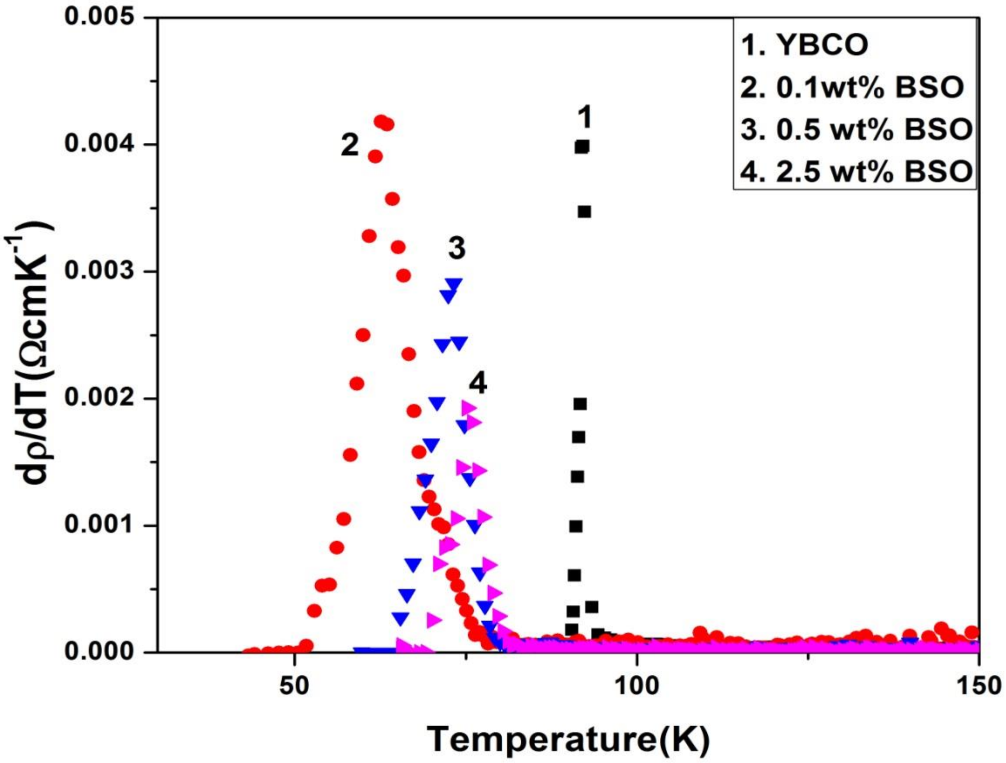

Fig.6 Temperature derivative of resistivity of YBCO + x BSO(x = 0.0, 0.1, 0.5, 2.5 wt. %) composites.

Table 1 Parameters calculated from derivative graphs

BSO(wt.%)	T_{c0}(K)	T_c(K)	ΔT(K)=(T_c -T_{c0})	P_{300}(K) (μ'Ω.cm)
0.0	90.24	92.04	1.8	3130
0.1	51.73	63.21	11.48	37730
0.5	64.53	73.10	8.57	18080
2.5	70.15	74.77	4.62	9660

From the above data it is clear that with increase in wt.% of BSO in YBCO the critical temperature T_c and T_{c0} increases gradually. It is found that T_{c0} increases and the transition width $\Delta T = T_c - T_{c0}$ decreases with increasing BSO content.

4.2 Microstructural analysis

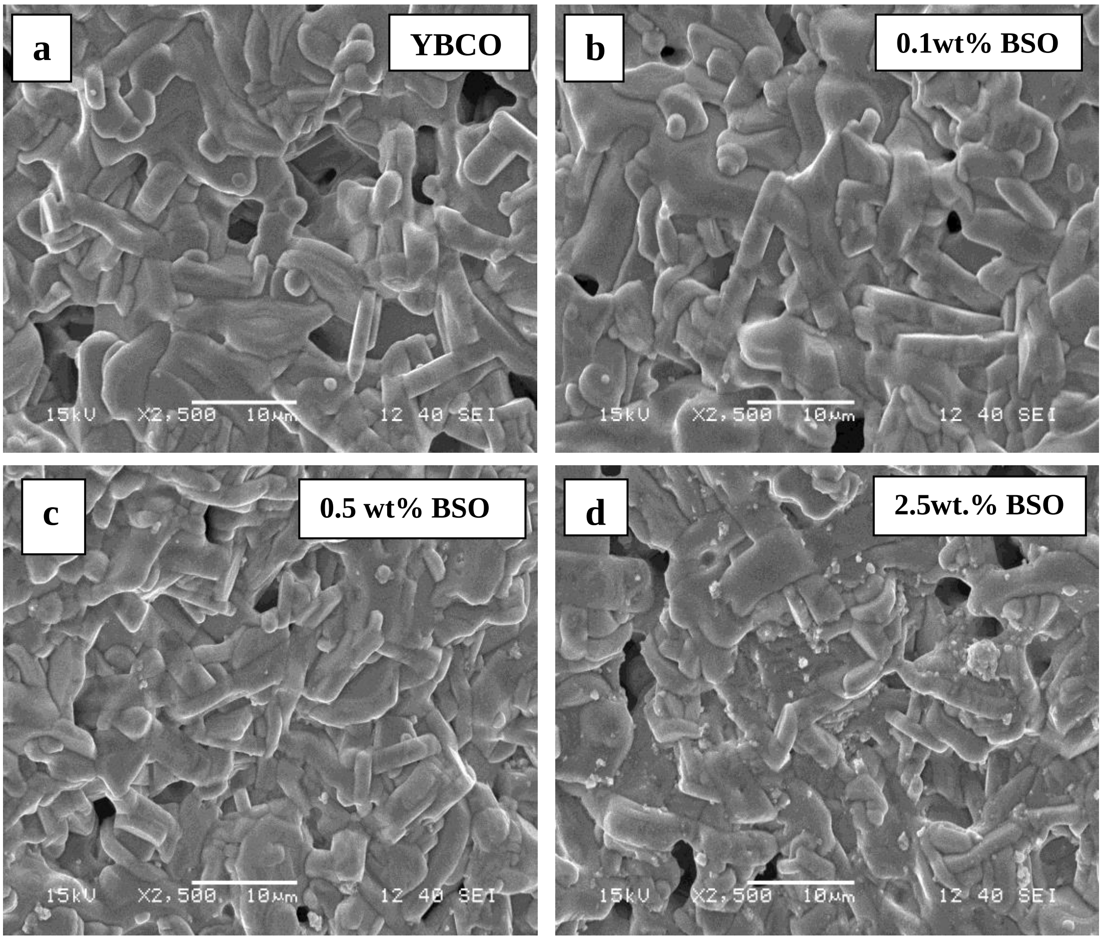

Fig.7 SEM micrographs of YBCO + x BSO composites (x = 0.0, 0.1, 0.5, 2.5 wt. %).

The microstructure characterization i,e, grain-size distribution of the composites as shown in Fig.7. It shows that pure YBCO sample exhibits large grains randomly oriented in all directions with varying size length. With addition of BSO there no such changes on microstructure are observed in fig 7(b and c). Extra deposition of BSO is observed between grains for 2.5wt % which may be accounted to excess addition of BSO. White dots of BSO are observed in fig 7(d).

CHAPTER-V

5. CONCLUSION:

From the R-T plot it is observed that T_c value increases with the increase in BSO weight percentage in the composites which affects the electrical transport property. T_c value increases upto 2.5 wt.%. Beyond 2.5 wt.% the graphs shows no transition. The normal state resistivity at 300K increases with BSO addition. Decreasing value of ΔT_c signifies that BSO addition affects the intergranular weak links. And there in on such change in grain size with the addition of BSO. The pinning properties of BSO can be utilized for enhancement of critical current density of the composite system.

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