

Ceramic-Ceramic Composite Superconducting Materials (YBCO-BaPbO₃) for Cryo-electronic Applications

ANAND K TYAGI

*Department of Applied Sciences (Physics & Materials Engg.),
SBS College of Engg. & Technology Firozpur – 152004 (Pb).
Phone: +911632 500791, Email: akt@aol.in*

The superconducting magnetic shields for cryo-electronic devices have been found to be more effective as compared to their conventional counterparts. However, the poor inter-grain connectivity in the ceramic high T_c superconductors like YBCO puts a serious limitation on their application potential in this area. YBCO superconductors doped with PbS have been investigated in this study and these are found to have 30-40 % improved shielding characteristics with greatly enhanced mechanical properties upto four times.

Key Words: Superconductors, HTSC, Magnetic Shielding, XRD, SEM/EDX

INTRODUCTION:

The performance of Cryo-electronic devices is impaired greatly by undesirable magnetic interferences and noise from various sources. Using the superconducting magnetic shields can alleviate it. The conventional shields of Pb & Nb suffer from intrinsic noise problem¹ as their operating temperature i.e. Liquid Helium Temperature (LHT) is sufficiently close to their superconducting transition temperature (T_c). This problem can, however, be eliminated by using high T_c superconducting materials. Of these, Yttrium Barium Copper Oxide (YBCO) is found to be relatively effective², but the major drawback with this material lies in its poor grain to grain connectivity³.

The Yttrium Barium Copper Oxide (YBCO) had been the most extensively investigated High T_c Superconducting system till date due to low refrigeration cost and easy tailoring of characteristics. There had been continuous efforts⁴⁻⁷ to improve its characteristics to have a dense microstructure with large grain size and small pore fraction to ensure better intergrain connectivity. It is envisaged that CuO plays a crucial role as far as properties of this superconductor are concerned⁷. Our recent report Tyagi *et al*⁶ investigates the Ag₂S doped YBCO system. Encouraged by the interesting findings of Ag₂S doping for CuO, we extended the study to other materials, having electric and dielectric properties similar to CuO. PbS is identified as a promising substitute for CuO in YBCO, keeping in view the resemblance in electric and dielectric properties of PbS and CuO⁸. The present work reports on the synthesis of YBCO

superconducting Ortho-phase in PbS doped YBCO superconductors and application of the synthesized materials in cryo-electronic shielding. The doping was found to reduce the intensity of grain boundary problem observed in pure YBCO superconductors⁹.

EXPERIMENTAL

We have investigated the YBCO-PbS superconducting system with nominal composition $[Y_1Ba_2(Cu_{1-x}Pb_x)_3S_{3x}O_y; x=0.0-0.1]$ and having T_c greater than Liquid Nitrogen Temperature (LNT) as shield materials for cryo-electronic applications. The magnetic shields in cylindrical shapes were fabricated using the pure YBCO and PbS doped YBCO superconductors, synthesized by the method mentioned in our earlier reports^{10,11}. The electrical characteristics of the samples were determined using Four Probe Technique discussed in reference¹⁰. Structural & microstructural aspects of the samples were analyzed in light of our earlier findings¹¹. The mechanical properties of the samples were determined by three point bend test using an Instron UTM. The shielding of an external dc magnetic field was measured at LNT by putting a calibrated Hall probe into the shield cylinders fabricated using the pure and PbS doped YBCO superconducting materials.

RESULTS AND DISCUSSION

The X-Ray Diffraction:

The diffractograms ($20 < 2\theta < 70$) for all the samples were recorded at room temperature. Fig.1 shows the XRD patterns of some of the samples prepared. The sample $x = 0$ showed peaks corresponding to orthorhombic symmetry. As the doping increases, some extra peaks start growing. The main impurity phases identified in the samples ($0.005 < x \leq 0.1$) are $BaPbO_3$ and Y-211 phase, however, $x > 0.1$ samples have $Y_1Ba_1Cu_2O_5$ (Y-112) insulating phase in low amount along with $BaPbO_3$. No detectable changes in positions of main 123 peaks is seen, however, one can easily observe a slight shift of (001) type reflections to lower 2θ values, which indicates a larger c-dimension in substituted compound, indicating the intake of larger S ion into YBCO matrix.

An interesting fact revealed by XRD results is that none of the possible impurity phases identified by us contains sulphur, hence sulphur has substituted for oxygen. However, the composition dependence of impurity peaks corresponding to $BaPbO_3$ suggests that most of the Pb of PbS has formed $BaPbO_3$, instead of substituting for Cu in YBCO matrix.

SEM/EDX Investigations

The microstructures of the samples coated with Au, were examined using SEM/EDX technique. Plate 1 displays the SEM photomicrographs of the surface of the sample $x = 0$ [a] and $x = 0.02$ [b]. It is found that the porosity typically

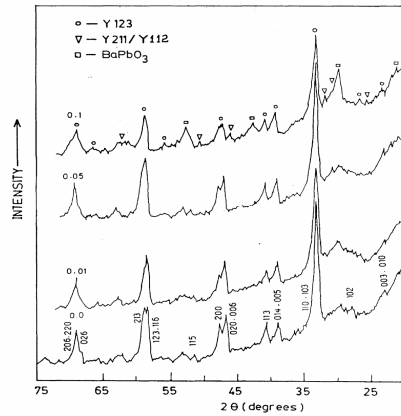


Fig.1: X-Ray Diffractograms of Extremities sintered YBCO-PbS samples showing BaPbO₃

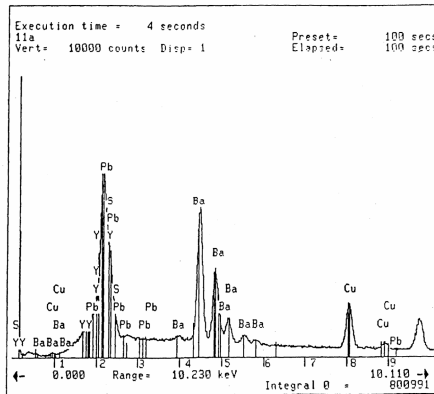
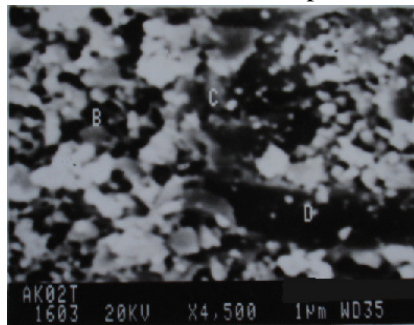
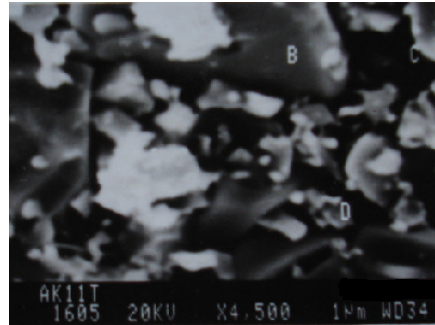


Fig.2: EDX Elemental Analysis of Grain in YBCO-PbS (x=0.02) sample

found in pure YBCO, is greatly reduced in doped sample ($x = 0.02$). The average grain size is also increased as a result of PbS doping. The typical grain size in undoped sample is 1-5 μm , whereas, in YBCO-PbS superconductor $x = 0.02$, it ranges from 4 to 10 μm . EDX analysis of these phases revealed that the big grains, with typical size 4-10 μm , are of Y-123 phase and the second phase BaPbO₃ is present near grain extremities (Fig.2) of this phase resulting into the microstructure similar to composites¹².



[a]



[b]

Plate 1: SEM Photomicrograph of Undoped [a] and doped (x=0.02) [b] YBCO sample

Resistivity Measurements:
 The results of dc electrical resistivity measurements on the sintered YBCO-PbS samples are shown in fig.3. Herein it can be seen that the samples having doping $x \leq 0.05$ have metallic normal state. These samples have mainly conducting phase BaPbO₃ as impurity. It has been found, on the other hand, that the samples $x=0.08, 0.1$ and 0.15 are semiconducting in their normal state and have impurity phases of BaPbO₃ and Y₂Ba₁Cu₁O₅ as revealed by XRD studies. The samples with still higher doping were insulating and non-superconducting and had the insulating phase Y₁Ba₁Cu₂O₅ also in small amount along with other impurities. Table 1 lists the superconducting and normal state properties of

the samples. The characteristic trend of variation in properties is due to the formation of conducting impurity phase BaPbO₃ which fills the pores between superconducting grains ensuring better intergrain connecting paths for electrical transport.

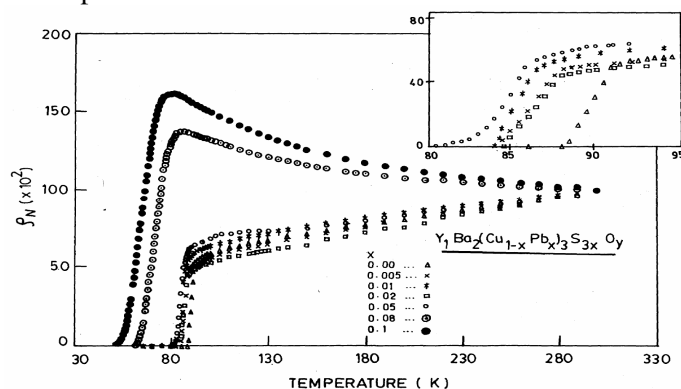


Fig. 3: Normalized Resistivity versus Temperature Plots for YBCO-PbS samples
Table 1: Normal state and superconducting properties of Y₁Ba₂(Cu_{1-x}Pb_x)₃S_{3x}O_y Superconductors.

x	Normal State Resistivity (300K) (10 ⁻⁵ Ohm m)	Rate of Change of Resistivity (10 ⁻³ Ohm m/K)	Transition Temp (T _c) (K)	Transition width (K)
0.00	2.41	1.86	90.2	2.0
0.005	1.84	1.76	87.2	2.0
0.01	0.98	1.54	85.8	0.8
0.02	1.63	1.58	86.75	1.5
0.03	1.97	1.83	85.55	1.8
0.05	2.33	2.35	85.4	1.9
0.08	17.98	\$	78.0	>2.0
0.10	97.13	\$	59.0	>2.0
0.15	Very High	\$	37.8	>5.0

\$ semiconducting behaviour.

Magnetic Shielding Measurements:

In order to evaluate these superconductors for magnetic shield materials, first the mechanical properties were studied. These materials were found to have improved mechanical properties (Fig.4), which is an essential requirement for good shield material after the good intergrain electrical contacts. The shielding of an external dc magnetic field measured at LNT by putting a calibrated Hall probe into the shield cylinders is shown in Fig.5. It was found that when the field was less than a certain Critical field H_s, The Hall probe registered no magnetic field within its limits of detection. The value of H_s for pure YBCO was found to be 275 Oe, with characteristic shielding curve.

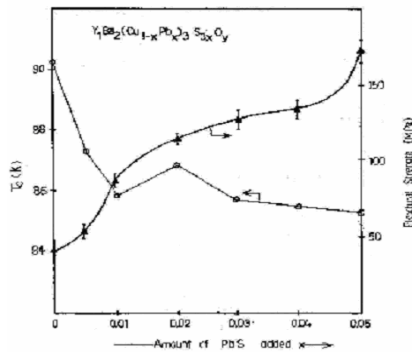


Fig.4: Mechanical properties & T_c of YBCO-PbS samples

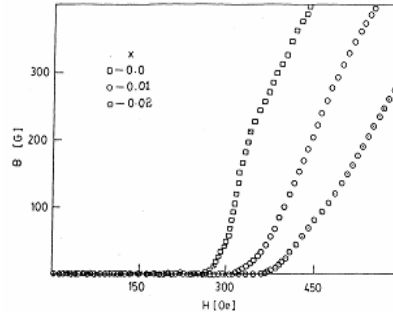


Fig.5: Shielding Characteristics of YBCO-PbS Tubular Shields

The YBCO-PbS shields indicated a drastic enhancement (30-40%) in H_s values. The magnetic field was also found to enter these shields relatively slowly. This clearly establishes that YBCO-PbS superconductors are the promising candidates to be used as shielding materials in Cryo-electronic applications with an additional advantage of lowering down the refrigeration costs as these operate at LNT instead of LHT in case of conventional shield materials.

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