

PROCESSABILITY AND METALLURGICAL REACTIONS DURING SINTERING IN YBCO-PbS SUPERCONDUCTORS

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Abstract

The YBCO-PbS superconductors have some interesting features, like better normal state and superconducting properties and enhanced shielding action towards magnetic fields. Present paper reports on the thermoanalytical and X-ray diffraction studies on these materials. The studies indicate that PbS addition enhances the synthesis of Y-123 Phase and lowers the temperature of partial melting of this phase which helps in reducing the voids. The metallurgical reaction occurring in sintering of PbS doped YBCO superconductors has been investigated and in light of the findings an explanation is given for the improved properties of these materials.

Keywords: DTA-TG, superconductors, YBCO-PbS superconductors, X-ray

Introduction

Utilization of high temperature superconducting materials in device application has been a challenge since their discovery. The root cause of the problem has been the poor grain to grain contacts leading to low mechanical strength and current density (J_c) in these materials. The recently reported [1] PbS doped YBCO superconductors (YBCO-PbS) have shown some interesting features [2, 3]. These include, a three fold enhancement in mechanical strength [2] for materials having superconducting transition temperature (T_c) above liquid nitrogen temperature (LNT). This enhancement may be even seven times for the samples with lower T_c values. These materials have shown an increased shielding action against the dc magnetic fields. A increase of 30-40% in magnetic field values that can be completely shielded using the cylinders of YBCO-PbS materials having T_c above LNT , has also been reported [3].

The X-ray diffraction (XRD) and scanning electron microscopic (SEM) studies reveal that the YBCO–PbS samples consist of the Y-123 phase containing sulphur as the host matrix wherein an additional phase BaPbO₃ with cubic structure not detected earlier in any YBCO superconductor, is also distributed near grain boundaries. Tyagi *et al.* [1–3] inferred that the peculiar characteristics of YBCO–PbS materials are due to this electrically active metallic ceramic phase.

In present paper we have investigated the processability of the YBCO–PbS superconductors and elucidated the metallurgical reactions, taking place during sintering. Simultaneous thermal analysis DTA/TG/DTG, along with powder X-ray diffraction have been employed in the present study.

Sample preparation and material synthesis

The YBCO samples with CuO partially substituted by PbS i.e. starting composition $(Y_2O_3)_{1/2}$, $(BaCO_3)_2$, $(CuO)_{3(1-x)}$ and $(PbS)_{3x}$ with $0 \leq x \leq 0.2$ (here x subscripts denote the molar contents of the starting compounds) were synthesized through solid state sintering route by taking stoichiometric amounts of starting materials having purity $\geq 99.99\%$. The starting powders were mixed thoroughly in an agate mortar. Simultaneous thermal analyser system Mettler TA-1 was employed to investigate the sinterability of the powder mix so obtained.

Although the preparation of the YBCO–PbS is similar to our method described elsewhere [1] a brief account is given here also. The samples were prepared by pelletizing the homogenised powders at 8 ton/cm² into tablet of roughly 8 mm dia and 6 mm height. These were then sintered at 910–950°C for 12–15 h depending upon the concentration of dopant in controlled dynamic oxygen atmosphere. Usually the heat treatment was repeated after regrinding and repelletizing the samples each time. The final sintering was, however, completed with annealing of all the samples at 560°C for 6 h and then furnace cooling.

Characterization

Powder X-ray diffractograms of the samples thus prepared were recorded on an ISO Debye Flex powder diffractometer model 2002 of Rich and Seifert Co., Germany, using CuK_α radiation. The dc electrical resistivity measurements were done using Montgomery four probe technique. The basic cryogenic system APD helium close cycle refrigeration cryostat of APD Cryogenics Inc., was used in these measurements. The scanning electron micrographs of the samples were taken on JEOL JSM 480A electron microscope equipped with energy dispersive X-ray microanalysis (EDX).

Result and discussion

Thermoanalytical investigations were performed in two phases, one with mixed starting powders to investigate the sinterability of the compositions and the other with sintered YBCO-PbS superconducting samples to see the nature of metallurgical reactions taking place. Both the experiments were done in dynamic oxygen atmosphere with 50 mg of sample and α -Al₂O₃ as reference material. The heating rate was 8 deg·min⁻¹. All other settings were kept the same throughout the study. DTA/TGA/DTG curves of the mixed starting powder for the undoped sample ($x=0$) is shown in Fig. 1.

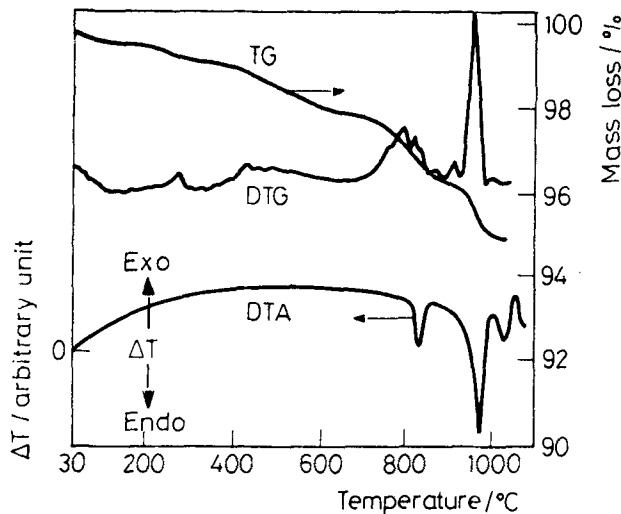


Fig. 1 DTA/TG/DTG curves of the undoped ($x=0$) starting powder mixture

The endotherms were observed in DTA at about 830 and 970°C which result from decomposition of BaCO₃ and partial melting of Y₁Ba₂Cu₃O_{7-z} respectively. The TG curve revealed approximately 0.5 mass % loss around 270°C which may be attributed [4] to the expelled absorbed gases, moisture etc. from the powder. The losses of 1.2, 1.8 and 1.5 mass % were observed at temperatures 510, 820 and 985°C respectively and these have been confirmed in DTG. The broad and gradual weight loss in the temperature range 510–800°C may be accounted for the expulsion of remaining gases from the powder mix and onset of decarbonation of BaCO₃. It is only the temperature beyond 800°C wherein the weight loss becomes very rapid. This effect is reflected in DTA curve also in which we get a sharp endotherm at 830°C. As we know that because of the catalytic action of CuO [5, 6] the decarbonation of BaCO₃ becomes very rapid around 820°C, the sharp endotherm observed at 830°C may be associated with

BaCO₃ decarbonation. The mass loss at 985°C is probably due to loss of oxygen from YBCO lattice.

One more important thing should be noted here that though we have a gradual weight loss in the temperature range 250–800°C but it does not signify any thermal event but removal of trapped gases from powder mix. Hence DTA trace alone describes almost completely the sequence of events taking place during sintering.

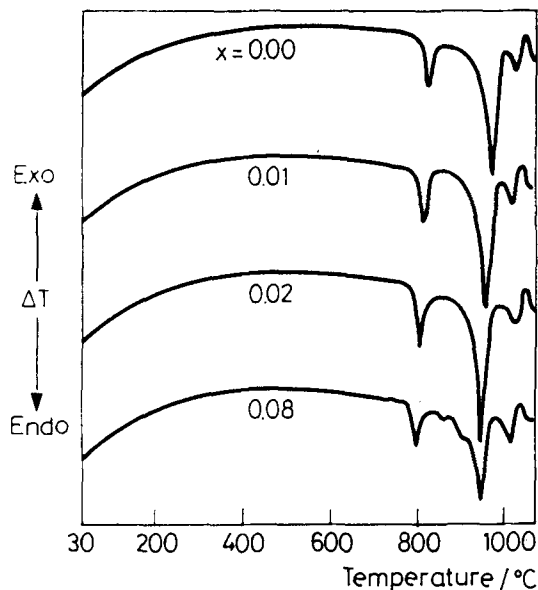


Fig. 2 DTA curves of the doped mixed starting powders

In the thermoanalytical curves of mixed starting powders of doped samples the endothermic DTA peaks as well as TG weight loss temperatures (especially 820°C) shift to lower values with increasing amount 'x' of PbS. Figure 2 clearly depicts the effect of doping on DTA endotherms. One can easily see that the decarbonation of BaCO₃ shifts to lower temperature by PbS addition. This effect in turn enhances the synthesis of Y-123 phase as evident by the larger area and increased sharpness of endotherm at 970°C for $x=0.02$ sample. The firing temperatures for different compositions were taken just 20°C below the temperatures of appearance of the endotherms corresponding to partial melting of YBCO and are shown in Table 1.

It is observed that if a composition is fired at the temperatures larger than specified in Table 1, a flux material comes out from the pellet and forms a thin layer on the bottom of platinum boat used for synthesizing the samples. The pellets so sintered were found insulating and very tough. The XRD results revealed

that such pellets were rich in Y_2O_3 . Therefore, it appears that $Ba_2Cu_3O_z$ melt [7] which could not get sufficient time to react with Y_2O_3 comes out of pellet leaving it rich in Y_2O_3 . Thus for proper phase development the temperature should not be higher than that mentioned in Table 1.

Table 1 Preparative aspects of the YBCO-PbS samples

Composition 'x'	Firing temp. / °C	Retention time / h
0.0	950	12-15
0.005	950	12-15
0.01	940	12-15
0.02	940	12-15
0.05	935	12-15
0.08	930	12-15
0.1	920	10-12
0.15	910	10-12
0.2	910	10-12

Note: (1) Heat treatment was repeated three times for all the samples

(2) Final heat treatment was followed by annealing all the samples at 560°C for 6 h

For the samples with PbS doping $x > 0.05$, the above mentioned effect of enhanced synthesis of Y-123 phase starts vanishing. The formation of impurity phases suppresses the synthesis of this phase. The evolved gas analysis (EGA) during these experiments did not indicate liberation of any gas containing sulphur, even in the sample with highest doping. This clearly reaffirms our earlier finding [1] that sulphur substitutes for oxygen in YBCO-PbS samples.

In the second phase of thermoanalytical investigations, we recorded thermograms of the synthesized YBCO-PbS samples. The results are shown in Fig. 2. The undoped sample ($x=0$) exhibits an endothermic peak at 1020°C only which is due to decomposition of Y-123 phase into Y-211 and liquid phases. As doping exceeds $x=0.01$, a new extra peak starts appearing around 970°C. With increasing PbS amount, the original peak at 1020°C starts shifting to lower temperature, while the newly grown peak remains unchanged. Two peaks completely overlap each other for the sample corresponding to $x=0.05$.

DTA results similar to Fig. 3 are obtained when Y-123 phase is mixed with different amounts of CuO, lowering of 1020°C peak to low temperature side and growth of a new peak around 970°C with increasing CuO amount are prominent. The temperatures corresponding to the two peaks are plotted as a function of PbS doped and CuO added to YBCO in Fig. 4. The scale of CuO content is twice that of PbS. With this modified scale the two sets of data resemble interestingly, which demonstrates that the amount of CuO required to have DTA

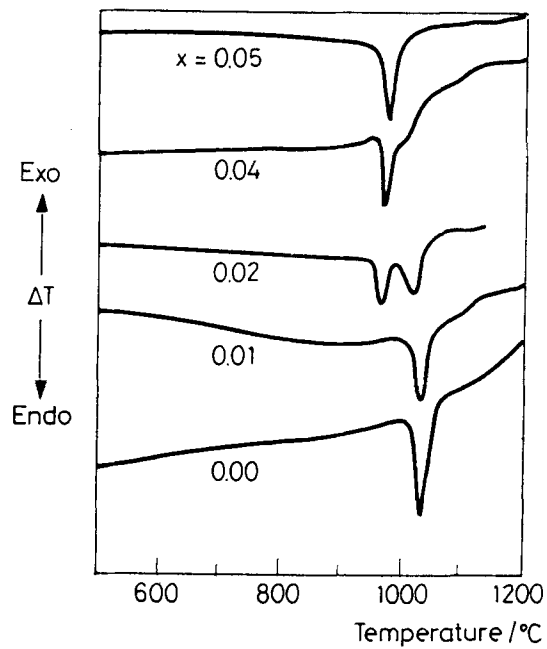


Fig. 3 DTA curves of the sintered YBCO-PbS samples

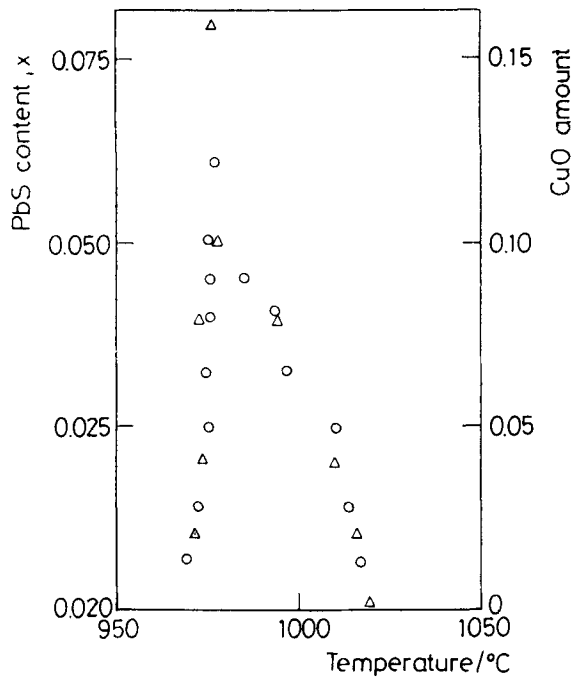


Fig. 4 Endothermic DTA peak temperatures vs. PbS doped and CuO added

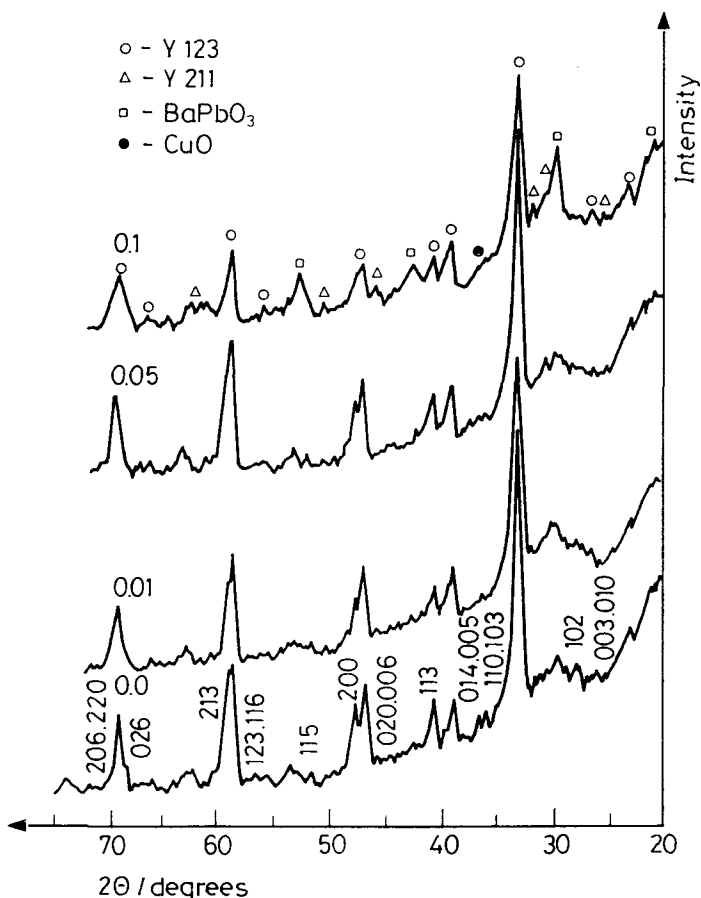
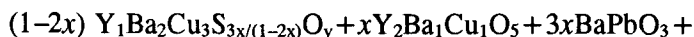


Fig. 5 X-ray Diffractograms of the sintered YBCO-PbS samples

peaks identical to that of YBCO-PbS corresponding to doping 'x', is '2x'. Keeping this fact in view and recalling that no sulphur containing impurity was detected in YBCO-PbS superconductors and that sulphur substitutes for oxygen whereas Pb does not substitute for copper in YBCO matrix [1], the metallurgical reaction occurring during sintering can be expressed as follows,



Here it is very easy to see that this equation reduces to the well known process for the formation of 123-phase in the case of $x=0$. We also confirmed that the sintering of Y-123 phase with appropriate amount of CuO results in similar thermotracess to ones obtained for YBCO-PbS compositions. One more interesting fact revealed by the DTA curves in Fig. 3 is that none of them indicated any thermal event upto the temperature of appearance of endotherms corresponding to partial melting of the samples, thus the phases of Y-211 and BaPbO₃ remain intact with the Y-123 phase.

XRD studies on the sintered YBCO-PbS materials (Fig. 5) indicated that samples $x=0$ and 0.005 showed diffraction patterns corresponding to orthorhombic symmetry. However, the samples ($0.01 \leq x \leq 0.05$) indicated formation of second phase BaPbO₃ along with orthorhombic Y-123 phase. Y₂Ba₁Cu₁O₅ (Y-211) and CuO are also detected in small amounts in the samples with $x > 0.05$. This finding further supports the metallurgical reaction (1).

The results of dc electrical resistivity measurements on the sintered YBCO-PbS samples (Fig. 6) indicated that the samples $x \leq 0.05$ have metallic normal state, on the other hand, the ones with still higher doping and having impurity phases Y-211 and CuO are semiconducting in their normal state. The results of resistivity measurement are listed in Table 2. One can easily assert from the table that normal state as well as superconducting properties show characteristic trend as doping increases. This effect owes to the formation of highly conducting ceramic phase BaPbO₃ that ensures better contacts among su-

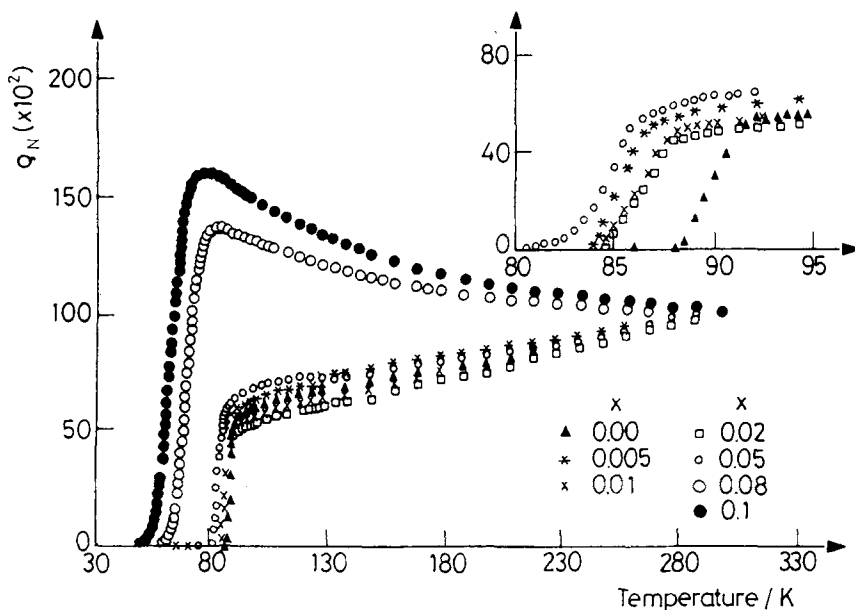


Fig. 6 Normalized resistivity vs. temperature characteristics of sintered YBCO-PbS

perconducting grains for electrical transport, as evident from the relatively high values of normal state conductivities for these samples ($0 < x \leq 0.05$). This effect along with enhanced synthesis of Y-123 phase, as revealed by thermoanalytical investigations, is responsible for the improved normal state, superconducting and magnetic shielding characteristics of these compounds.

Table 2 Room temperature resistivity $\rho_{300\text{ K}}$, transition temperature T_c , transition width ΔT_c and rate of change of resistivity with temperature in normal state ($d\rho/dT$)_{ns} for YBCO-PbS samples

x	$\rho_{300\text{ K}} /$ $10^{-5} \Omega\text{m}$	$(d\rho/dT)_{\text{ns}}^*$ $10^{-5} \Omega\text{m}\cdot\text{K}^{-1}$	$T_c /$ K	$\Delta T_c /$ K
0	2.41	1.86	90.2	2.0
0.05	1.84	1.76	87.2	1.9
0.01	0.98	1.54	85.8	0.8
0.02	1.63	2.35	86.75	1.5
0.05	2.33	1.58	85.4	1.9
0.08	17.98	#	78.0	> 2.0
0.10	97.13	#	59.0	> 2.0

* $(d\rho/dT)_{\text{ns}}$ is calculated from linear $\rho(T)$ vs. T plot in the temperature range ($1.5 T_c \leq T \leq 300\text{ K}$)

$(d\rho/dT)$ is negative and continuously changing, semiconducting behaviour

Conclusions

PbS doping is doubly advantageous as it makes the starting oxides to yield the metallurgical reaction (1) and considerably lowers the requisite temperature for Y-123 phase development. The sintered YBCO-PbS samples show prompt partial melting of superconducting phase at relatively lower temperature which is essential to reduce voids. Secondly the conducting second phase BaPbO₃ ensures better intergrain electrical contacts and hence improved properties.

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Zusammenfassung — YBCO-PbS Supraleiter verfügen über einige interessante Eigenschaften, wie zum Beispiel bessere Eigenschaften im normalen als auch supraleitenden Zustand und eine erhöhte Abschirmungsaktivität gegenüber magnetischen Feldern. Vorliegender Beitrag berichtet über thermoanalytische und Röntgendiffraktionsuntersuchungen an diesen Materialien. Die Untersuchungen zeigen, daß der Zusatz von PbS die Bildung der Y-123-Phase steigert und die Temperatur von partiellem Schmelzen dieser Phase herabsetzt, was Hohlräume mindert. Die metallurgische Reaktion beim Sintern von mit PbS versetztem YBCO Supraleiter wurde untersucht und angesichts der Ergebnisse eine Erklärung für die verbesserten Eigenschaften dieser Materialien gegeben.