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ISOTHERMAL SINTERING, MICROSTRUCTURE AND SUPERCONDUCTING

PROPERTIES OF $Y_1Ba_2Cu_3O_{7-x}$ COMPOUND

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A B S T R A C T

The polycrystalline $Y_1Ba_2Cu_3O_{7-x}$ material was prepared by the solid state reaction method and characterised by X - ray powder diffraction method, Meissner effect, resistivity by four probe method and iodometric titrations. Well characterised material was processed at $(930 \pm 5)^{\circ}C$ and the isothermal sintering behaviour upto 96 hrs have been studied using different experimental techniques such as positron lifetime, X - ray powder diffraction, scanning electron microscopy (SEM), four probe method for resistivity and critical current measurements as a function of magnetic field and differential thermal analysis (DTA). Two types of grain morphology are observed by SEM, one below 36 hrs and another above 36 hrs of sintering. The DTA studies show one peak around $954^{\circ}C$, above 36 hrs of sintering. The positron lifetime results reveal that the lifetime values τ_1 and τ_2 arise from the positron trapping in the strained / deformed regions and microvoids formed in the triple defect junctions (TDJ), respectively. The size of the defect responsible for the pinning centres is estimated from the positron lifetime data. The reasons for the lesser value of transport J_c ($24.72 A/cm^2$), obtained in the $Y_1Ba_2Cu_3O_{7-x}$ compound sintered at $(930 \pm 5)^{\circ}C$ are explained. The nature of defects related to the resistivity component in the $Y_1Ba_2Cu_3O_{7-x}$ compound are also discussed .

I N T R O D U C T I O N

After the discovery of superconducting properties in the La - Ba - CuO ceramic oxide compound by Bednorz and Muller [1], many new compounds in this family such as La - Sr - CuO, Y - Ba - CuO, Bi - Ca - Sr - CuO and Tl - Ca - Ba - CuO have been synthesised [2 - 5]. Eventhough materials with superconducting transition temperature T_c more than 100 K have been reported, many researchers are still actively engaged in the study of Y - Ba - CuO system, considering it as a model system, (i) to improve the mechanical properties like compression strength, fracture toughness, microhardness, for the construction of high field magnets which requires the processing of materials into long, flexible wires, (ii) to investigate the formation of new superconducting and non superconducting phases developed during the processing, (iii) to find the causes for the low values of transport critical current density J_c , critical magnetic fields H_{c1} & H_{c2} [6 - 8]. The distorted, perovskite - like orthorhombic superconducting phase $Y_1Ba_2Cu_3O_{7-x}$ with X values from 0.1 to 0.5 is formed from the mixture of Y_2O_3 , $BaCO_3$ or BaO and CuO at temperature between 900 - 930°C by the solid state reaction method followed by sintering at or around this temperature in oxygen atmosphere for 24 hrs and an oxygen annealing either by slow cooling from this reaction temperature or around 400 - 500°C for 10 to 15 hrs [9,10]. The compound undergoes a linear phase transition from orthorhombic ($0.1 < X < 0.5$) to tetragonal symmetry ($X > 0.5$) at 700°C and vice versa [11]. During this time large number of intrinsic and extrinsic defects were produced [12].

Sintering is one of the powder metallurgical technique used for densification of particles after hydrostatic pressing to get the required mechanical and physical properties [13]. The $Y_1Ba_2Cu_3O_{7-x}$ powders can be consolidated via. solid state, liquid phase sintering and hot pressing [14]. Of the three, liquid phase sintering which occurs in the liquid - solid interface produces better densification than other types of sintering because of the filling of liquid in the pores in between the grains. The topology of the grains may change during this process [15]. Partial melting of this compound above $940^{\circ}C$, which is well below the incongruent melting point, has been observed by many workers [16,17]. The melting point of this compound is $1010^{\circ}C$ by incongruent process to form Y_2BaCuO_5 + liquid phase [18]. The ternary peritectic reaction $Y_1Ba_2Cu_3O_{7-x} + CuO \rightarrow Y_2BaCuO_5 +$ liquid at $940^{\circ}C$ is responsible for the partial melting, single crystal growth and synthesis of pure polycrystalline compound [19]. Single crystals having dimensions less than a few mm were grown in the temperature region $925 - 960^{\circ}C$ by many crystal growers [20,21]. One group reports that the partial melting above $940^{\circ}C$ is due to the reaction between $BaCuO_2 - Y_1Ba_2Cu_3O_{7-x}$ binary joints and $BaCuO_2 - CuO - Y_1Ba_2Cu_3O_{7-x}$ ternary joints [22]. In DTA studies, in between the temperature region $900 - 1150^{\circ}C$, two endothermic peaks were developed from the powder calcined once at $925^{\circ}C$, which is well below the peritectic reaction point. First peak onset around $940^{\circ}C$ and second around $1114^{\circ}C$ [19,23]. The evidences of glassy like nature present in this compound was observed from the mechanical properties like elastic modulus, microhardness and fracture toughness [24]. The transport J_c value

in the densed polycrystalline material is very low and is of the order of $10 - 450 \text{ A/cm}^2$, whereas in the melt textured samples J_c is around $1.7 \times 10^4 \text{ A/cm}^2$, in the single crystals $1 \times 10^4 \text{ A/cm}^2$ in zero applied magnetic field at 77 K [25,26]. The grain size dependence on the J_c in the polycrystalline material was studied and it was found that the grain size and the J_c was inversely related on application of the magnetic field [27]. The J_c value in the ball milled specimen on sintering in the temperature region $925 - 960^\circ\text{C}$ was $10 - 15 \text{ A/cm}^2$, whereas in the calcined specimen in the same temperature region was $35 - 80 \text{ A/cm}^2$ [28]. Generally the presence of impurities and variation in composition of the superconducting phases affect the sharpness of the T_c , H_{c1} & H_{c2} , whereas other structural / extended defects having sizes around the coherence length improve the J_c [29,30]. The observed defects present in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound are oxygen vacancies in the basal plane (a - b plane), reflection twins in (110) plane, rotation twins in (001) plane, anti-phase domain boundaries, superstructures, microcracks, dislocations, stacking faults, grain boundaries, amorphous strips and precipitated phases [31 - 33]. But still the nature of defect that influences the J_c in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound is not well understood.

Positron annihilation spectroscopy is one of the well known non-destructive probe to analyse the nature of defects, even the sizes less than 2A° , which is not possible by other microscopic techniques such as SEM, TEM, HREM, etc. [34]. Number of positron annihilation studies on the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound have been carried out by many workers [35-39]. The reported lifetime values are 210 - 220 psec by Jean et al. [35], 193 - 199 psec by Liolios

et al. [36], 196 - 223 psec by Shoji Ishibashi et al. [37], and 190 psec by Bharathi et al. [38]. Wang et al. reported that the observed lifetime values 193 - 203 psec are due to the average lifetime of positrons trapping in the lattice defects and free state annihilation [39]. Mandal et al. reported that the lifetime value 153 psec is responsible for the annihilation in the CuO_2 layers [40] and 333 psec in the copper ions which involved in the superconducting properties [41]. Kjeld O. Jenson calculated the positron lifetime values under different possible conditions in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ system and estimated 170 psec in oxygen vacancy present in the basal plane, 207 psec in Cu(1) vacancy, 182 psec in Cu(2) vacancy, 206 psec in Y vacancy, 263 psec in Ba vacancy and 236 psec in Cu(1) - O(1) divacancy complexes [42].

Overall survey of the literature mentioned in the references indicate that the superconducting properties were highly affected between the temperature regions viz., (i) 500 - 700°C and (ii) 925 - 960°C during the preparation and processing of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound. The authors have investigated the isothermal sintering behaviour of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound at the temperature $(930 \pm 5)^\circ\text{C}$, which is very near to the peritectic reaction of this compound. Main probe used for this study is positron lifetime technique aiming to correlate the defects and microstructure to J_c . Other experiments such as X - ray powder diffraction, four probe method for T_c & J_c , SEM and DTA have been used to characterise the synthesised $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound.

EXPERIMENTAL PROCEDURE

1. Preparation and characterisation of the starting material:

a) The compound $Y_1Ba_2Cu_3O_{7-X}$ was prepared by the standard solid state reaction method [43] from the mixture of 99.99 % purity Y_2O_3 , $BaCO_3$, and CuO . Repeated grinding and heating in air at $(930 \pm 5)^\circ C$ for 24 hrs by resistive heating method were done to yield uniform mixture of the resultant compound. The chemical reaction to form the $Y_1Ba_2Cu_3O_{7-X}$ phase from the mixture is as follows:

The resultant compound was well ground and circular pellets of dimensions 1 cm in diameter and approximately 1.5 mm in thickness were obtained with a hydrostatic pressure of 4.5 Kbar (1 bar = 10^5 pa.).

An oxygen annealing of the specimens was done for 12 hrs at $(930 \pm 5)^\circ C$, cooled slowly to $500^\circ C$, treated at that temperature for 12 hrs and cooled to room temperature slowly. In order to get the superconducting phase, $X < 0.5$, flow of oxygen was found to be necessary.

One such pellet was ground and the X - ray powder diffraction was made using $Cu K_{\alpha}$ radiation. The X - ray results confirmed that the prepared compound was pure orthorhombic crystal structure having the cell dimensions $a = 3.8184 \text{ \AA}$, $b = 3.8968 \text{ \AA}$ and $c = 11.6988 \text{ \AA}$, which agreed well with the literature values [44,45].

- b) Meissner effect was tested at liquid nitrogen temperature.
- c) The oxygen content in the compound was found to be 6.9 from the iodometric titration experiment.
- d) The zero resistance temperature was found by specially designed four probe method (experimental details are given in the experimental procedure section) and the observed value was 95 K.

Similar size pellets, as explained earlier, were prepared from the well characterised powders and sintered at $(930 \pm 5)^{\circ}\text{C}$ for 12 hrs, 24 hrs, 36 hrs, 48 hrs and 96 hrs in oxygen atmosphere. Further experiments were carried out using the above sintered specimens.

2. Positron lifetime technique:

The positron lifetime studies were measured using a fast - slow coincidence system [46]. The resolution of the spectrometer was estimated using ^{60}Co radioactive isotope in the ^{22}Na energy window. The full width at half maximum of the ^{60}Co spectrum was 260 psec. The positron source was prepared from an aqueous solution of ^{22}Na deposited on a thin aluminium foil ($1.13 \text{ mgm} / \text{cm}^2$) and folded. The source thus prepared was sandwiched between two identical samples of dimensions 1 cm in diameter and 1.5 mm in thickness. Ambient temperature (22°C) measurements were carried out with as - compacted and also with sintered pellet specimens. The data were analysed using the POSITRONFIT program [47]. The source component was subtracted from the total spectrum during analysis. The experimental data were analysed for two and three lifetime components after the source correction. The results obtained from the two component

fit were found to have minimum χ^2 values. The lifetime parameters such as lifetime values τ_1 & τ_2 with intensities I_1 & I_2 and average lifetime value $\bar{\tau}$ [48] are given in Table 1 and the data are graphically shown in figure 1.

3. Resistivity and critical current measurements:

Four probe method with specially made sample holder was used for both resistivity and critical current density measurements [49]. The block diagram of the sample holder is shown in figure 2. Four press contacts were made on the sample by spring loaded system. For good electrical contact, gold vapour coating with silver paste was made on the sample. Heat treatment was given in an oxygen atmosphere at the four contact points to achieve better interface between the sample and silver paste. The size of the sample used was 1 cm in length and 3 mm in width. Resistivity and critical current measurements were made in all the sintered specimens. Figures 3 & 4 show respectively, the temperature dependence of the resistivity and J_c at 4.2 K against applied magnetic field for all the sintered specimens. The resistivity at T_c onset point and the zero field J_c value at 4.2K are shown in figures 5 & 6 respectively.

4. X - ray powder diffraction studies :

All the X - ray patterns, except step scans, were taken under similar experimental conditions. Before taking the X - ray pattern, all the sintered specimens were ground to get narrow distribution of particle size. The cell dimensions calculated for all the sintered specimens are given in Table 2 and the

corresponding diffraction patterns are shown in figure 7. The step scans taken between the Bragg angles $\theta = 15 - 17^\circ$ are shown in figure 8.

5. Differential thermal analysis:

The DTA studies were performed for all the sintered specimens with the following experimental conditions : oxygen atmosphere = 35 mbar, scan rate = $10^\circ\text{C}/\text{minute}$, temperature range = $600 - 1150^\circ\text{C}$ and weight of the sample = 13 mgm. The figure 9 shows the DTA spectra.

6. Scanning Electron Microscopy:

The scanning electron microscopy Model JSM - 35 CF having resolution $60 \text{ \AA}$ was used to study the microstructure especially grain morphology in the as - compacted and sintered specimens. The figures 10a & 10b show the SEM photographs of the surface and the fractured regions of the as - compacted and figures 10c to 10h show the fractured regions of the sintered specimens, respectively.

RESULTS AND DISCUSSIONS:

RESULTS:

The positron lifetime value τ_1 in the as - compacted specimens is 193 psec whereas in the sintered specimens upto 36 hrs of sintering the τ_1 values are almost constant around 170 psec (fig. 1a). The lifetime value τ_2 is constant, equal to 388 psec, in the as - compacted and sintered specimens upto 36 hrs of sintering (fig. 1b). During this period the mean lifetime value $\bar{\tau}$ in the as - compacted specimens is 240 psec. It scatters between 205 - 207 psec (fig. 1c) for the samples sintered upto 36 hrs. Above 36 hrs, τ_1 , τ_2 and $\bar{\tau}$ values increase from 169 psec to 200 psec, 388 psec to 428 psec and 206 psec to 226 psec, respectively (figs 1a - c). The lifetime intensity I_2 , corresponding to the lifetime value τ_2 decreases with sintering time (fig. 1e).

The resistivity at the T_c onset point decreases from $17 \times 10^{-3} \Omega \cdot \text{cm}$ for 12 hrs to $1.5 \times 10^{-3} \Omega \cdot \text{cm}$ for 36 hrs and remains almost constant upto 96 hrs of sintering (fig. 5). All the sintered specimens show zero resistivity around 95 K and the exact values of the T_c and J_c at zero field are given in Table 2. The J_c value at 4.2 K with the applied magnetic field $B = 0$ T increases from 10.00 A/cm^2 for 12 hrs to 24.72 A/cm^2 for 36 hrs and remains almost constant upto 96 hrs of sintering (fig. 6). Since the J_c values were constant after 36 hrs of sintering, one of the sample sintered at 36 hrs was reheated in oxygen atmosphere for 24 hrs at 500°C . After this treatment, the J_c value increases to 84 A/cm^2 at zero field. This value is the maximum value obtained in our specimens sintered at $(930 \pm 5)^\circ\text{C}$.

Imanaka et al. report a J_c value of 88 A/cm^2 in zero field for polycrystalline $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound.

The powder X - ray results show that all the sintered specimens are orthorhombic crystal structure with well defined 013 and 110/103 line splitting (fig. 8). From the X - ray diffraction results, no impurity lines or multiphase lines were observed upto 96 hrs of sintering. In the DSC experiments two endothermic peaks, one onset around 1014°C and another around 1080°C were developed in the sintered specimens below 36 hrs (fig. 9). But in the sintered specimens at and above 48 hrs, in addition to the above said two peaks, development of a new peak around 954°C was seen (fig. 9). This observation implies that eventhough the X - ray results do not indicate any impurities, the DSC measurements are sensitive to these impurities.

From the SEM study, two types of grain morphology were observed upto 96 hrs of sintering viz., first one upto 36 hrs of sintering and second above 36 hrs of sintering. In the first type, the grains were seen to grow with increasing neck contacts to form strained continuous chains (figs. 10c & 10d). In the second type a new pattern of morphology was formed (figs. 10e - g). During this period a lot of transcrystalline fractures were formed which would increase the density of microcracks (fig. 10h).

In the following paragraphs the reasons for the changes in the grain morphology, possible positron trapping centres, decrease in the resistivity at T_c onset point, types of defect

responsible for pinning centres and the low value of J_c are discussed.

DISCUSSIONS:

The sintered powder materials are likely to be strained / deformed in four ways viz., (i) grinding, (ii) hydrostatic pressure applied for consolidation, (iii) sintering and (iv) presence of possible impurities as indicated by the DSC results. The possible defects developed due to the above four process are dislocations, lattice distortions, weak microcrystalline interfaces, pores and microvoids [50]. Each polycrystalline particle contains an agglomeration of number of microcrystals having weak interface regions.

Initially the surface grains in the as - compacted specimen are in the form of uneven rectangular sized grains ranging from 2 - 4 μm (fig. 10a) whereas in the fractured regions, the grains are found to be in the form of dumb bell shape (fig. 10b). This statement indicates that the surface grains of the pellet specimens were deformed by the applied hydrostatic pressure. The volume compressibility is found to be 14.6 Kg/mm^2 by a separate experiment [51].

On sintering, the grain growth occurs at the expense of smaller grains, reduction in the microcrystalline interface regions by the migration of interface boundaries, by increasing the inter - grain contact regions. This is the first stage in the solid state sintering [52]. During this period necks were developed in between the neighbouring grains. As the inter -

grain bridges (necks) grow, they will form isolated pores, shrinkage of which results in the increase of the density of the compact. This is the second stage in the solid state sintering [52]. The above two stages have occurred in our system upto 36 hrs and are clearly seen in the SEM photographs (figs. 10c - d). Due to the formation and growth of neck regions, more lattice regions were strained / deformed in the interfaces as well as within the grains. The basal plane (a - b plane) is also one of the distorted region within the crystal system [31]. The HREM and TEM studies have shown that in most of the grains the basal planes are facing the grain boundary and microcrystalline interface surfaces [53,54]. From the above, the authors deduce that the strained regions present in this material are (i) grain surfaces, (ii) microcrystalline interfaces and necks formed in the inter - grain regions and (iii) basal plane . Except the pore regions all the surfaces were bridged with adjacent grains. Since the inter - grain interfaces, microcrystalline interfaces and basal planes were formed in the same regime, they mix together to form a junction or joint named as triple defect junction (TDJ). Due to this mixture new defects like dislocation jogs, dislocation kinks and microvoids followed by point defects might have originated. Since the necks were formed only after sintering, there is no such possibilities to the formation of TDJ in the as - compacted specimens.

After 36 hrs of sintering, the pattern of the grain morphology was rearranged from the specimens sintered below 36 hrs, which might be due to the coexistence of liquid phase and solid state sintering [55]. The changes generally occur during

this period are reorientation of solid grains, filling of materials in the free volume defects, nucleation of new phases or decomposition due to chemical reaction between the neighbouring atoms, etc. The DTA result shows an onset of a new endothermic peak around 954°C above 36 hrs of sintering. There are reports showing formation of liquid phase at 950°C from BaCuO_2 - $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ binary joints and BaCuO_2 - CuO - $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ ternary joints [22]. The X-ray pattern of all sintered specimens do not indicate any impurity lines probably due to low concentration. From this the authors presume that the rearrangement in the grain morphology is due to the melting of low concentration of impurities present in the compound which may diffuse through the interface and pore regions to create more strains around the interface regions. The changes in the positron lifetime parameters on sintering and the possible positron trapping centres in this compound are discussed in the following section.

From the figure 1 the lifetime value τ_1 (193 psec) in the as - compacted specimens is higher than that in the sintered specimens (≈ 170 psec), below 36 hrs. The lifetime value τ_1 is due to the annihilation of positrons in the perfect region of $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound, as well as lattice defects such as vacancies or dislocations or both. Thus τ_1 represents the mean lifetime of both perfect site, τ_c , structural vacancies, τ_v and dislocations, τ_d [56]. The developments of more lattice strains / deformations in the interface regions on sintering were explained in the microstructure analysis section. Due to this lattice strains / deformations more vacancy type defects are

expected to be developed in the interfaces in addition to the line defects and microvoids. Since the interface regions were very weak compared to the interior sites, migration of vacancies into the interior sites by displacing the atoms to the interfaces might have occurred [52]. This could have in turn built more bridges between the grains. This atomic migration improves the electron charge density in the interface regions. As there is an inverse relation between electron density and positron lifetime [57] more positrons annihilate in the interface regions on sintering, which is reflected as the lesser value of τ_1 (≈ 170 psec) in the sintered specimens below 36 hrs. But the lifetime values τ_2 ($= 388$ psec), which is equal to the lifetime of microvoids [58], is constant both in the as - compacted and sintered specimens upto 36 hrs. However, I_2 decreases on sintering which can be assumed as an indication of reduction of pores or microvoids by the process discussed above. The microvoids formation in the TDR might be due to the intersection of inter - grain interfaces, microcrystalline interfaces within the grains and Cu - O layer formed in the basal plane, which was explained earlier.

Above 36 hrs of sintering both lifetime values τ_1 and τ_2 increases with sintering. This increase in the value of τ_1 can be explained as in the previous paragraph. After 36 hrs of sintering, increase in the value of τ_2 and decrease in the value of I_2 with an increase in τ_1 are noted. This situation seems to be possible only if some of microvoids grew at the expense of smaller voids. Comparing the positron lifetime results with the microstructure on sintering, the authors feel that there is

enhancement of the electron charge density in the interfaces through the atomic migration mechanism.

It is worth to make a comparative study of defects and microstructure with the superconducting properties. Eventhough new defects and reorientation in the microstructure were developed on sintering as explained earlier, the T_c remains almost same ($= 95$ K) in all the sintered specimens. This implies that the superconductivity in the $Y_1Ba_2Cu_3O_{7-x}$ compound is insensitive to the microstructure and defects. The decrease in the resistivity at T_c onset point from $17 \times 10^{-3} \text{ } \Omega\text{-cm}$ to $1.5 \times 10^{-3} \text{ } \Omega\text{-cm}$ on sintering is due to the decrease in the defect scattering centres related to the resistivity component. But the positron lifetime and microstructure results show atomic defect density increases on sintering. Hence it is found that the defect responsible for the electron scattering centres which is related to the resistivity component are different from the defects observed from the positron lifetime study. At the same time J_c increases with sintering. The J_c depends only on the processing history of the material; it is not characteristics of an element, an alloy or compound [59]. Also the samples with the defect size much smaller or much larger than coherence length ξ , exhibit reduced pinning centres. That is, the magnetic fluxes are pinned only if the defect size is around the coherence length [60]. Thus the present positron lifetime results and microstructure results indicate that the defects like vacancies and lattice strains, due to their sizes smaller than ξ , do not contribute much to the magnetic flux pinning. The reported value of the ξ in the $Y_1Ba_2Cu_3O_{7-x}$ compound is around $5A^\circ$ [24]. The

presence of microdefects, with the size around this coherence length, in the $Y_1Ba_2Cu_3O_{7-x}$ compound can be predicted from the positron lifetime parameter, τ_2 . These microvoids having size around ξ_1 formed in the TDJs can be responsible pinning centres. From figure 1 it is seen that the I_2 parameter which is a measure of microvoid concentration decreases on sintering. However the J_c which is directly related to the pinning centres (in our case the microvoids of size ξ_1) increases with sintering time. This is an indication that the microvoids tend to have narrow size distribution around ξ_1 . The increase in the J_c values from 10.00 A/cm^2 to 24.72 A/cm^2 on sintering is due to the increase in the concentration of electron charge density in the interface regions which builds more bridges between the neighbouring grains. The order of J_c values observed in our pellet specimens sintered at $(930 \pm 5)^\circ$ is same as the other reported results [8,28] for the polycrystalline specimens sintered around the same temperature.

The very low value of J_c (24.72 A/cm^2) obtained in our specimen may be due to the weak bridges [16,61] between the interfaces, less concentration of ξ_1 size defects, and the presence of other impurities on the surface of each grains.

CONCLUSIONS:

In conclusion the following results are obtained from the $(930 \pm 5)^\circ\text{C}$ isothermal sintering behaviour of the $Y_1Ba_2Cu_3O_{7-x}$ compound.

1. The continuous chain like morphology formed in the fractured regions changes above 36 hrs of sintering.

2. The new endothermic peak onset around 954°C , obtained from the DTA study, which is around the peritectic reaction of the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound, is due to the partial melting of the compound. During this period the molten precipitates diffuse through the interfaces and cover the pores and change the grain morphology above 36 hrs of sintering.
3. The cell dimensions calculated from the X - ray diffraction patterns show that $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ is stable in orthorhombic state upto 96 hrs of sintering.
4. The presence of superconductivity in the present compound on sintering upto 96 hrs with a constant value of T_c ($= 95 \text{ K}$) shows that in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$, the superconducting behaviour is insensitive to the microstructure and defects.
5. The positron lifetime parameter τ_1 shows the formation of more vacancy type defects in the interfaces on sintering.
6. The decrease in the I_2 parameter on sintering is due to the decrease in concentration of microvoids in the TDR. However the microvoids tend to have narrow size distribution around the coherence length ξ .
7. The increase in the J_c values on sintering is due to the increase in the concentration of electron charge density in the interface regions. The microvoids with around the ξ , are the possible pinning centres in the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ compound.

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FIGURE CAPTIONS

1. Positron lifetime parameters τ_1 , τ_2 , $\bar{\tau}$, I_1 , and I_2 of the $Y_1Ba_2Cu_3O_{7-x}$ as a function of sintering time. Solid lines are only for guidance.
2. Block diagram of the sample holder arrangements for the four probe set - up (1. Spring loaded press contacts, 2. Movable glass holder, 3. Sample, 4. Copper plate and Sapphire base, 5. Copper block, 6. Fe - Rh resistance thermometer, 7. Double coiled heating element).
3. Temperature dependence of the resistivity for $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time.
4. Magnetic field dependence of the critical current density J_c of the $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time.
5. Resistivity values at T_c onset point for $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time.
6. Critical current density J_c values at 4.2 K with $B = 0$ T for $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time.
7. X - ray powder diffraction patterns of the $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time (Bragg angles, $\theta = 10 - 35^\circ$).
8. X - ray powder diffraction pattern of the $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time (Bragg

angles, $\theta = 15 - 17^\circ$).

9. DTA curves for $Y_1Ba_2Cu_3O_{7-x}$ heat treated at $(930 \pm 5)^\circ C$ for different sintering time.

10 (a,b).

SEM photographs of the as - compacted $Y_1Ba_2Cu_3O_{7-x}$ a: surface and b: fractured regions (both 2000 mag.).

10 (c-h):

SEM photographs of the fractured regions in the sintered $Y_1Ba_2Cu_3O_{7-x}$ specimens heat treated at $(930 \pm 5)^\circ C$ for c: 12 hrs, d: 24 hrs, e: 36 hrs, f: 48 hrs, g : 96 hrs and h: 96 hrs. (c - g : 2000 mag. h : 10,000 mag.).

Table 1. Positron lifetime parameters of the $Y_1Ba_2Cu_3O_{7-x}$ as a function of sintering time.

Sintering time in hrs	τ_1 (psec)	τ_2 (psec)	I_1 (%)	I_2 (%)	$\bar{\tau}$ (psec)
0	193	386	75.30	24.70	240.67
12	169	386	82.70	17.30	206.54
24	171	387	82.92	17.08	207.89
36	169	388	83.17	16.83	205.85
48	173	404	85.40	14.60	206.72
60	175	409	86.05	13.95	207.64
72	185	417	86.53	13.47	216.25
84	188	420	87.32	12.68	217.41
96	200	428	88.60	11.40	225.99

Table 2: Lattice parameters, T_c and J_c with $B = 0$ T values of the $Y_1Ba_2Cu_3O_{7-x}$ as a function of sintering time.

Sintering time in hrs.	a ($\text{\AA}$)	b ($\text{\AA}$)	c ($\text{\AA}$)	T_c (K)	J_c (A/cm^2) at 4.2 K with $B = 0$ T
12	3.818	3.896	11.698	95.0	10.10
24	3.820	3.894	11.697	94.7	17.86
36	3.825	3.896	11.699	95.0	24.72
48	3.826	3.898	11.699	96.5	24.07
96	3.828	3.897	11.700	94.6	23.61

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 6

Fig. 5

Fig. 7

Fig. 8

(10a)

→
(10b)

(10c)

→
(10d)

(10e)

(10f)

→ (10x)

→ (10x)

Fig. (10a-b)

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