EFFECT OF SILVER ON THE SINTERING CHARACTERISTICS OF HIGH T_c CERAMIC SUPERCONDUCTORS

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ABSTRACT

A detailed investigation on the densification behaviour of Y-Ba-Cu-oxide (YBCO)-Ag_x and Bi-Pb-Sr-Ca-Cu-oxide (BPSCCO)-Ag_x composite powder synthesised by a chemical pyrophoric decomposition technique is made. It has been observed that Ag plays a significant role on the lowering of sintering temperatures and melting points of these superconductors. In YBCO-Ag_x, for $0< x\leq 0.6$ the rate of densification increases and for $0.6<x<1.2$ the rate of densification decreases. The densification behaviour is due to oxygen absorption at the interface of YBCO and Ag grains and a low temperature eutectic Ag_2O_x formed which promotes liquid phase sintering. Studies on the sintering characteristics under inert atmosphere indicate increased densification with the silver addition. The removal of oxygen from Ag_2O_x to the inert sintering atmosphere enhances the densification rates. This is also confirmed from the weight loss of the pellets observed in the TG experiments. Sintering studies of BPSCCO-Ag_x composites show decrease of densification with the Ag content in the matrix. The degradation of superconducting properties is attributed to the change of chemical compositions of the composites. The evaporation loss of Bi, Pb, Sr and Cu during sintering is observed to be the cause of degradation. The evaporation losses are increased with x.

Key Words :

Ceramic superconductors, YBCO, BPSCCO, Composites and Silver

1.0 INTRODUCTION

Since the discoveries of the ceramic superconductors in Y-Ba-Cu-oxide (YBCO) system in 1987 [1] and Bi-Sr-Ca-Cu-oxide (BSCCO) system in 1988 [2], the research activities are increased extensively to use these materials for various industrial applications. In this direction voluminous research works have been carried out on the metal-ceramic composites and anticipated to be used in high current carrying conductors, wires for superconducting magnets and interconnects. However, most of the common metals are found to be reactive with these superconductors. Amongst the metals, silver and gold have been found to be less reactive and thus addition of silver has been studied extensively. It has been observed that silver improves densification, grain growth and mechanical properties of the superconductors [3,4]. In contradiction to many observations, silver has also been observed to degrade the superconducting properties and also have been found to replace Cu in the YBCO lattice [5] and silver is also reported to wet the YBCO grains above 1203 K [6]. Similar results have also been reported for the BSCCO superconductors, where both improvement [7, 8] and degradation have been mentioned [9].

Though extensive literature are available on the addition of Ag to these materials, the densification behaviour of these materials are not discussed properly. In the present paper, an attempt has been made to understand the role of Ag on the densification behaviour of YBCO and Bi-Pb-Sr-Ca-Cu-oxide (BPSCCO) superconductors.

2.0 EXPERIMENTAL

In this investigation , YBCO-Ag_x ($x = 0, 0.2, 0.6, 0.8, 1.0, 1.2$) powders with a nominal composition of Y:Ba:Cu:: 1:2:3 and BPSCCO-Ag_x ($x = 0, 1, 2, 5$ & 10 wt%) with a composition of Bi: Pb: Sr: Ca: Cu:: 1.4:0.6: 2 : 2 :3 were prepared by chemical pyrophoric reaction technique. The detail of the process has been published elsewhere [10]. The synthesised YBCO and BPSCCO powders were calcined at 900°C and 800°C respectively. Silver powder was added in different ratio as mentioned above and after mixing the powder were pelletised into 2.54 cm diameter disc by applying a pressure of 12.4 MPa. The rectangular pieces of YBCO were cut and sintering behaviour were carried out using a thermomechanical analyser (Stanton, UK) either in air or nitrogen atmosphere. BPSCCO pellets were sintered at 845°C for 96 hours in air and nitrogen atmosphere. Densities of the samples were measured by Archimedes principle using liquid immersion technique. Sintered specimens were characterised by XRD, SEM-EDX. Superconducting properties of the sintered compacts were also investigated using a close cycle heluim cryo-refrigerator. Thermal analysis (TG and DTA) of the powders were also carried out to study the thermal behaviour of these materials.

3.0 RESULTS AND DISCUSSION

Sintering behaviour of YBCO-Ag powder compacts

The synthesised YBCO-Ag_x powder was observed to be a dual phase material consisting metallic silver and orthorhombic YBCO (123 phase). The XRD analyses of the YBCO-Ag_x powder (calcined at 900°C and soaked for 1h) indicate that the crystallites are less than 100 nm in size and the submicrometre sized particles observed in the TEM investigation suggest that the particles are weakly agglomerated.

TMA studies of the YBCO-Ag powder compacts show that the samples undergo shrinkage above 800°C and the onset of shrinkage which is indicative of the initiation of sintering, is decreased with the addition of Ag. Typical sintering curves of YBCO-AgO and YBCO-$Ag_{0.2}$ powder compacts showing the continuous variation of length with time and temperature is shown in Figure 1. This shows expansion and contraction of the samples during heating & cooling and significant shrinkage during sintering. The variation of apparent densities of the samples sintered for 1h at various temperatures are shown in Figure 2. The densification behaviour of the samples are observed to vary with the increase of silver concentration and the silver is also observed to play a significant role on the lowering of the sintering temperatures and the melting points of YBCO-Ag_x composites. The densities of the samples increase continuously for $0<x\leq0.6$ and then decrease on further increase of silver concentration in the range of $0.6<x\leq1.2$. The weight loss of the powder compacts during sintering studied by the TG experiments revealed that the weight loss increases upto $x\leq0.6$ and then on further increase of x, the weight loss decreases (Fig. 3). The weight loss is due to the oxygen desorption from the YBCO during sintering which control the vacancy concentrations and thus the rate of densification. Silver in proximity of YBCO grain absorbs oxygen from the YBCO and creates more vacancies as a result the mass transfer is increased to facilitate more densification. Oxygen absorption at the interface of YBCO and Ag grains also led to the formation of a low temperature eutectic (Ag_2O_x) which promotes liquid phase sintering. With higher silver concentrations the mass transfer is possibly affected by the sluggish diffusion of oxygen from the matrix to the environment. However, the cause of such behaviour is not clearly understood.

SEM studies of the samples indicate fine particles of YBCO grains and formation of silver globules (Fig. 4). The size and quantity of silver globules increase with the increase of silver (Fig. 4). Optical micrograph of the sample indicates the existence of metallic silver outside the YBCO grains (Fig. 5). The silver at the vicinity of YBCO grains modifies the weak-link from S-I-N-S to S-N-S and improve the transport properties. The variation of densities of the YBCO-Ag_x samples sintered in nitrogen atmosphere is shown in Figure 6. Studies on the sintering characteristics under inert atmosphere indicate increased densification with the silver addition. Here, the fast removal of oxygen from Ag_2O_x to the sintering atmosphere i. e. nitrogen, enhances the densification rates. This is also confirmed from the weight loss of the pellets observed in the TG experiments

Sintering behaviour of BPSCCO-Ag powder compacts

AC susceptibility measurements of the BPSCCO-Ag_x pellets sintered in air at 845°C for 96h is shown in Figure 7. From the figure it is evident that the transition due to 2223 (110K) phase is continuously decreased with the increase of Ag content. It is also evident that 2212 (80K) phase is increased in the BPSCCO-Ag_{1x} samples at the expense of 2223 phase and total superconducting phase is also decreased. The degradation of superconductors is possibly due to interaction of Ag with BPSCCO and is thermally characterised by the DTA experiments. The variation of melting peak of the BPSCCO-Ag_x samples is shown in Figure 8. The melting peak is observed to decrease with the addition of increasing amounts of Ag. This lowering of melting point may possibly be accounted for by the following :

a) Metallic silver has been known to cause partial reduction of CuO to Cu_2O and Cu_2O forms a eutectic with PbO,

and b) Ag-O-CuO-Cu_2O-PbO forms a low melting eutectic.

The formation of these low melting eutectics also causes significant loss of various cations excluding CaO at the sintering temperature, possibly through evaporation, as can be seen from Figure 9. The composition of the pellets has been determined by EDX analysis and the average value of the composition determined at various points and normalised for Ca = 2.0 has been reported. The variation of densities of the sintered BPSCCO-Ag_x pellets is shown in Figure 10. The degradation of 2223 phase has resulted in significant reduction of densities of the samples when sintered in air. The absence of low temperature Ag-O-CuO-Cu_2O-PbO eutectic in nitrogen atmosphere is observed to cause less evaporation of the constituents and the densities are not affected significantly. However, due to low oxygen content high T_c (i.e. 2223) phase is not formed and thus the densities are not improved remarkably.

AC susceptibility measurements and X-ray diffraction analyses indicate that, on sintering the silver containing samples at 845°C for 96h, a drastic decrease in the formation of 2223 phase occurs. SEM image of BPSCCO-Ag_2 pellet shows that platelet nature of growth observed in BPSCCO-Ag_0 samples was absent (Fig. 11). The onset of superconducting transition of BPSCCO-Ag_5 was at 75K which is lower than 80K of 2212 phase. The same superconducting sample showed transition at 80 K after annealing in nitrogen atmosphere (Fig. 12). The lowering of T_c to 75 K was possibly due to excess oxygenation of the samples leading to increased oxygen content in Bi-O plane on account of oxygen desorption by silver.

Conclusion

The role of Ag on the sintering characteristics of YBCO-Ag and BPSCCO-Ag superconductors is investigated. Silver plays a significant role on the lowering of sintering temperatures and forms a low temperature eutectic in YBCO-Ag composites which promotes liquid phase sintering. The densification increases continuously for $0<x\leq0.6$ and then decreases on further increase of x. Densification of YBCO-Ag pellets increases with the silver content due to easy oxygen diffusion from the matrix to the sintering environment in inert atmosphere.

Lowering of melting point in the silver added BPSCCO composites enhances the rate of evaporation of the constituents as a result degrades the superconducting, densification and microstructural properties.

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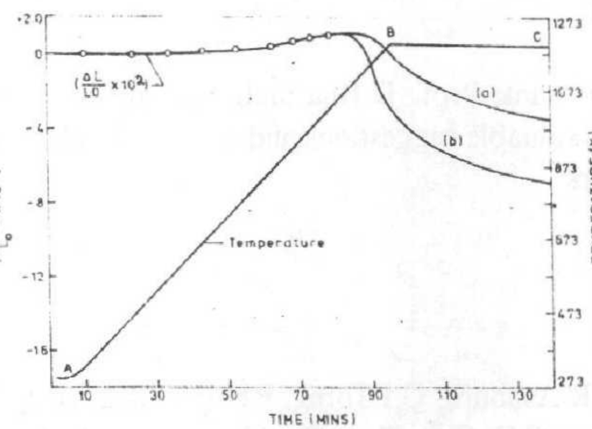

Fig. 1 - Typical sintering curves for the samples : a) YBCO-Ag_0 and b) YBCO $Ag_{0.2}$ in air atmosphere.

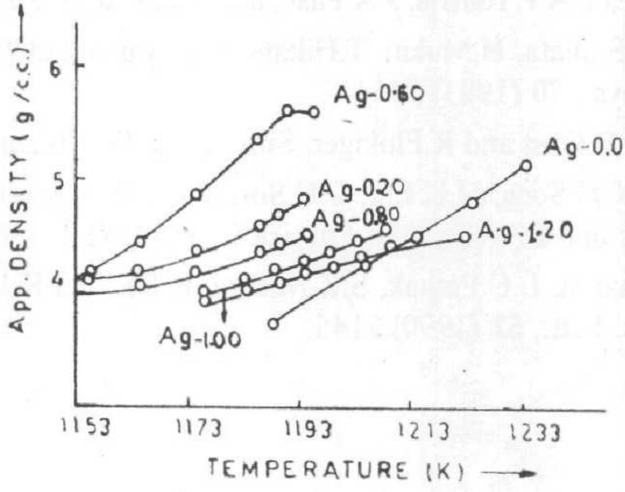

Fig. 2 - Variation of apparent densities of the YBCO-Ag_x samples sintered in air for 1h at various temperatures.

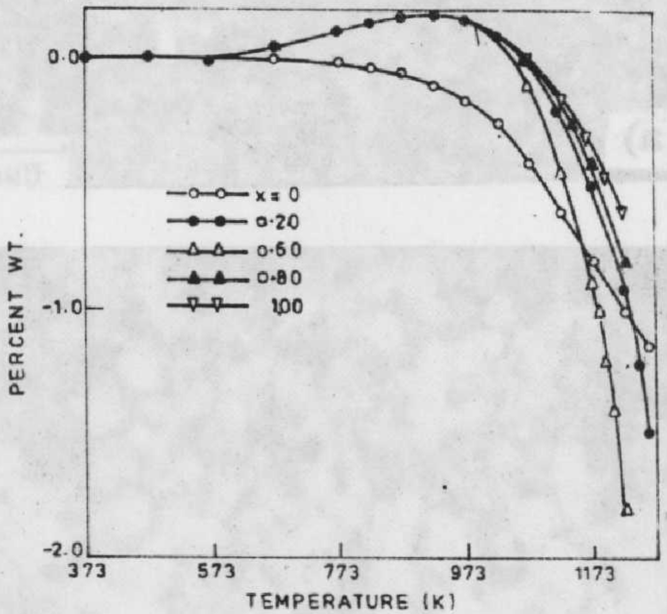

Fig. 3 - TG Thermogram of the YBCO-Ag_x samples in air.

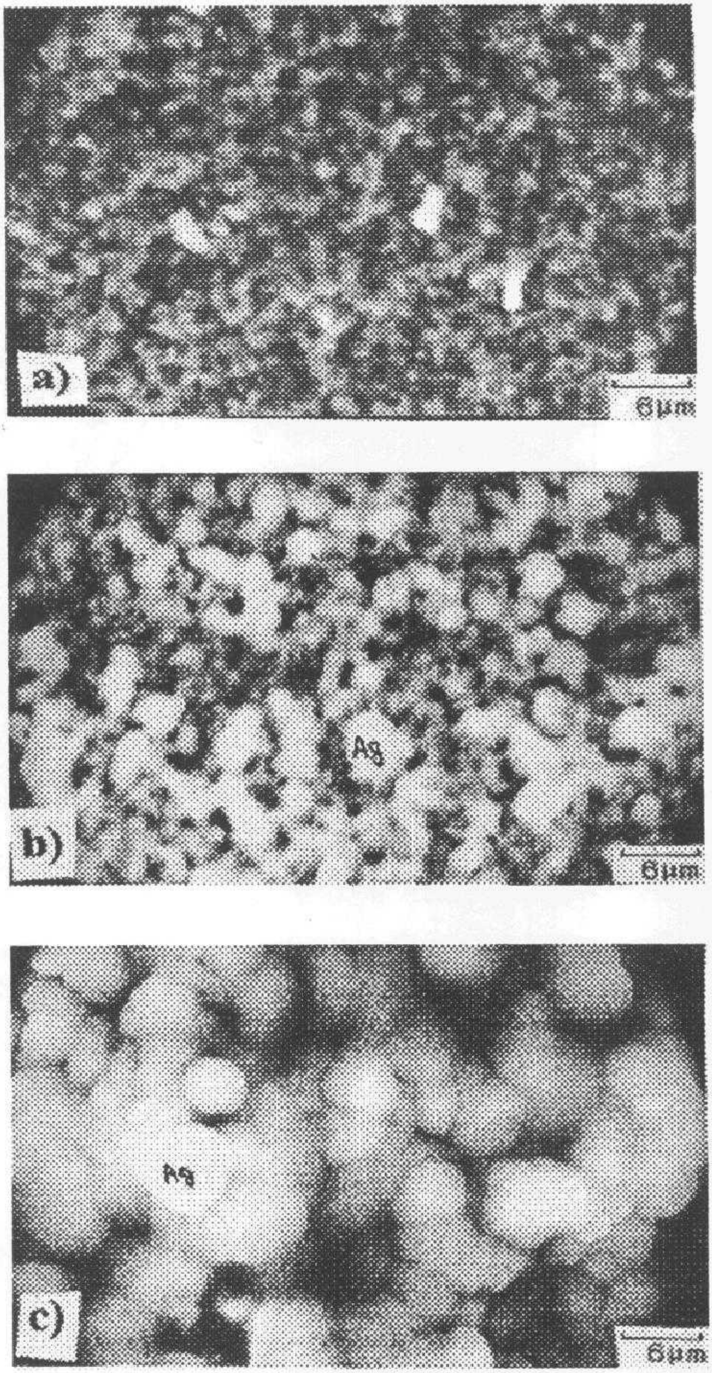

Fig. 4 - SEM images of YBCO-Ag_x pellets sintered at 900°C for 1h
a) x = 0, b) x = 0.6 c) x = 1.2

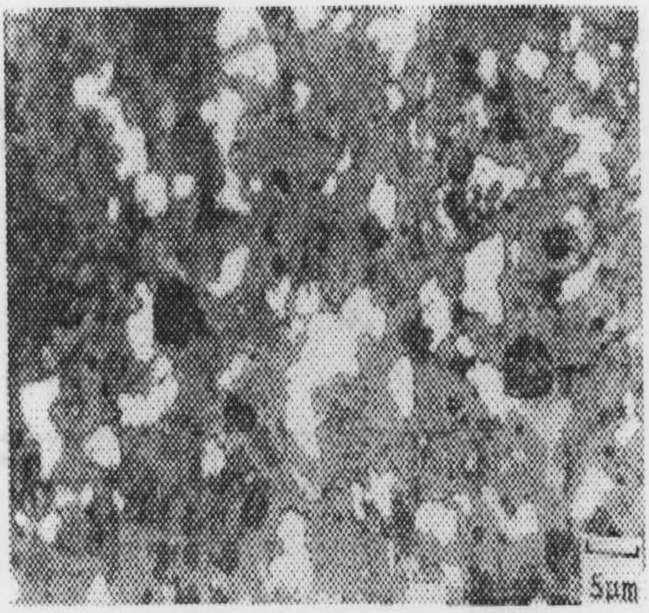

Fig. 5 - Optical micrograph of YBCO-$Ag_{1.2}$ pellet sinter for 1h at 980° C in air.

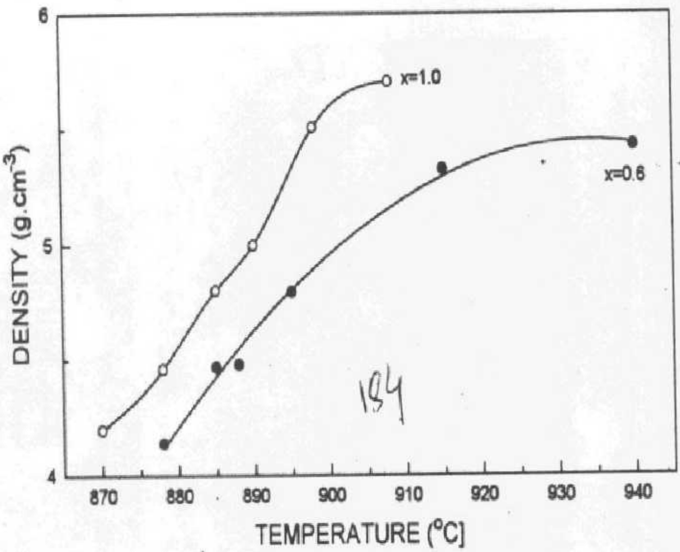

Fig. 6 - Variation of YBCO-Ag_x samples sintered in Nitrogen.

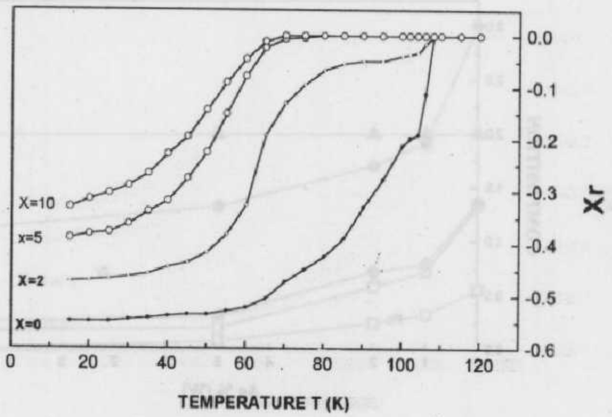

Fig. 7 - Variation of AC susceptibility of BPSCCO-Ag_x pelletes with temperature.

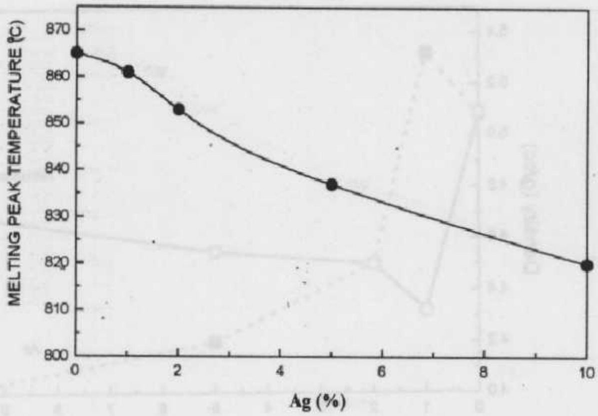

Fig. 8 - Variation of melting peak temperature with Silver concentration.

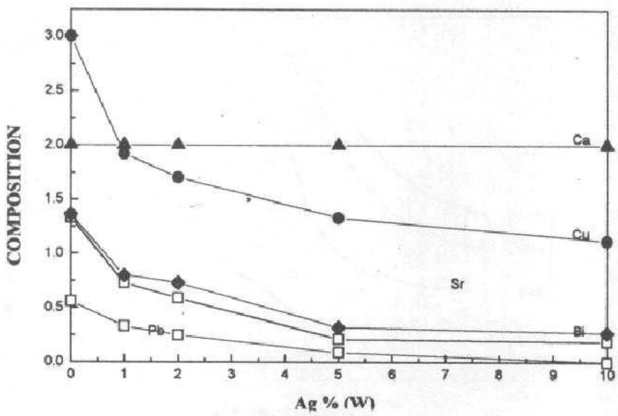

Fig. 9 - Variation of composition of BPSCCO pellet with silver concentration

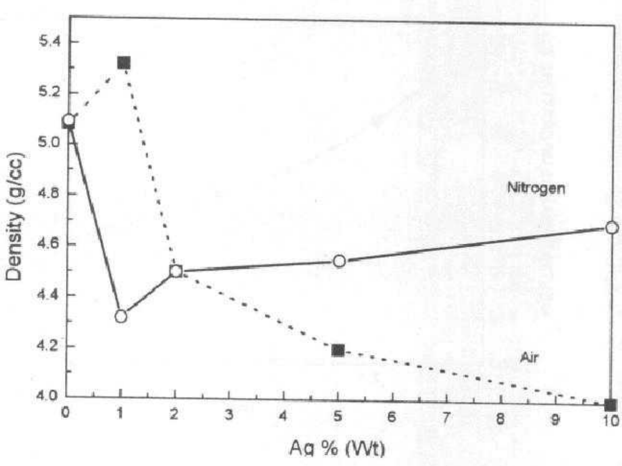

Fig. 10 - Variation of density with Ag concentration.

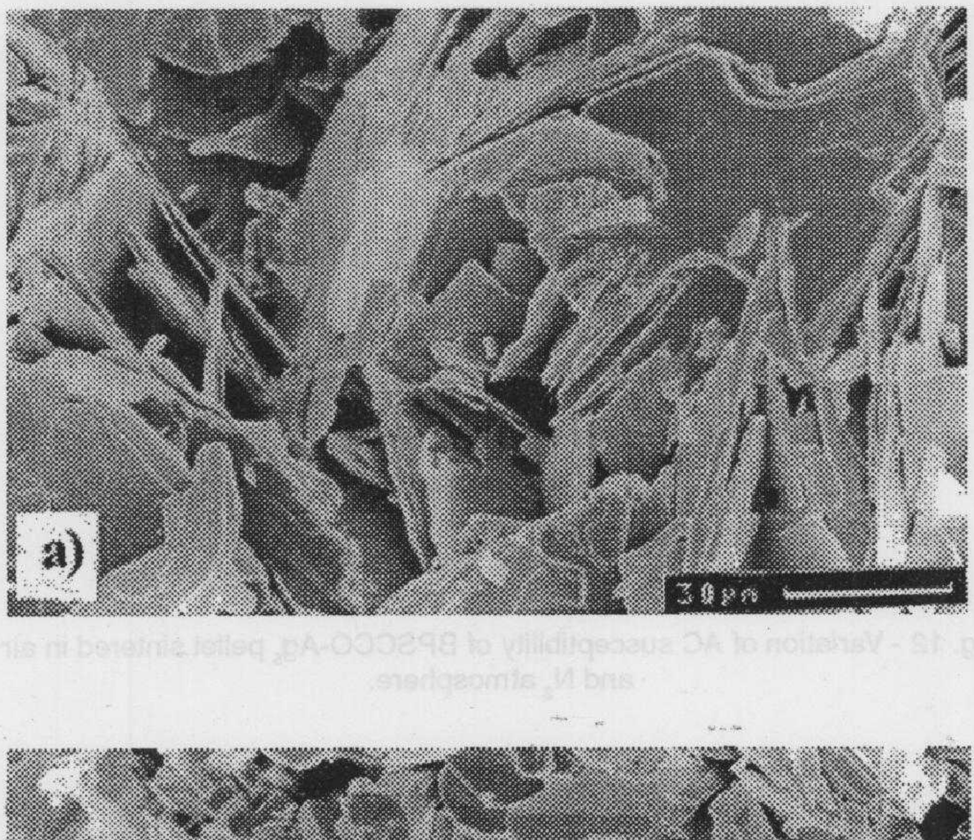

Fig. 11 - SEM images of BPSCCO-Ag_x pellet sintered at 845° C for 96h in air a) x= 0 and b) x = 2.

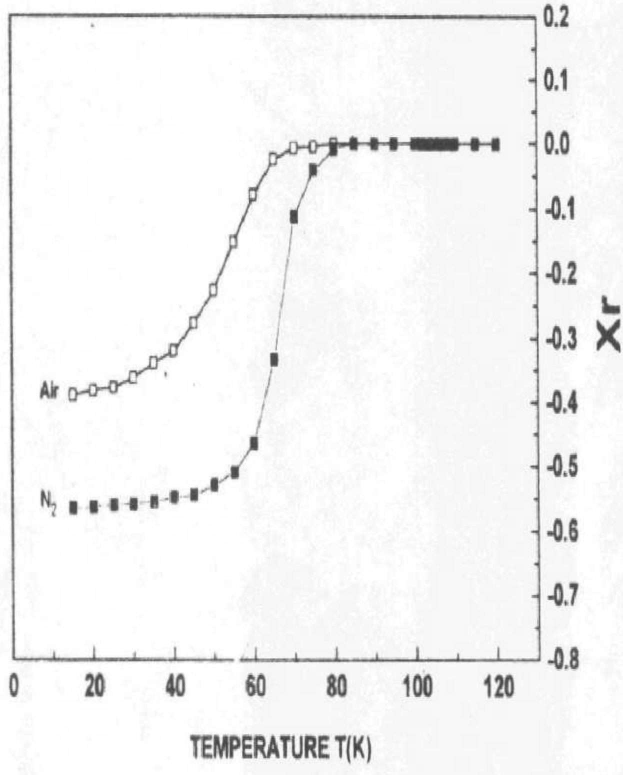

Fig. 12 - Variation of AC susceptibility of BPSCCO-Ag_5 pellet sintered in air and N_2 atmosphere.