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COMMUNICATION I

Onset of Orthorhombic-tetragonal Structure in $(YBa_2Cu_3O_{7-\delta})_{1-x}(SnO_2)_x$ Superconducting Ceramics

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ABSTRAK

Superkonduktor suhu tinggi, $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ dengan x berubah dari 0.00 hingga 0.06 telah disediakan dalam udara di bawah keadaan pensinteran yang optimum. Kesuperkekonduksian dan titik mula peralihan struktur ortorombik - tetragonal dibincangkan berdasarkan kepada hasil kajian belauan sinar-X. Kesan Meissner pada suhu melebihi suhu cecair nitrogen dicerap untuk semua sampel dan ini menunjukkan pengekalan struktur ortorombik di dalam sistem berlaku sehingga penggantian Sn sebanyak 6%.

ABSTRACT

High T_c superconductors, $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ with x ranging from 0.00 to 0.06 were prepared in air under optimum sintering conditions. Superconductivity and the onset of orthorhombic-tetragonal structure are discussed in relation to the results of X-ray diffraction studies. Meissner effect above liquid nitrogen temperature was observed for all the samples, suggesting the retention of orthorhombic structure in the system up to 6% Sn substitution.

INTRODUCTION

Following the discovery of superconductivity in the Y-Ba-Cu-0 system (Wu *et al.* 1987), numerous researchers began to explore the feasibility of substituting different elements into the $YBa_2Cu_30_{7-\delta}$ structure. To date, some degree of lattice substitution has been achieved on each site in the structure. Part of the initial enthusiasm for substitutions came from the possibility of further raising the superconducting transition temperature (Murphy *et al.* 1987: Nishi *et al.* 1988). More recent studies have focused on the structural, valence and magnetic effects of cation substitution in an effort to understand the relevance of various structural features to superconductivity. Several clear issues have emerged from these studies, of which the most important is the unique square planer Cu-atoms each surrounded by 4 or 6 oxygen atoms and crucial to the superconductivity observed in oxides (Izumi *et al.* 1987). The aim of this work is to focus on the effect of interstitial substitution of Sn in the $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ system for x = 0.00 to 0.06. There are not many papers reporting on the effect of Sn substitution on the materials (Suzuki *et al.* 1988; Paulose *et al.* 1991) compared to other dopants (Suzuki *et al.* 1988; Mikhailov *et al.* 1990).

MATERIALS AND EXPERIMENTAL METHODS

In this work, $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ compounds were prepared by the solid-state reaction method using an appropriate mixture of 99.99% pure Y_20_3, $BaC0_3$, Cu0 and $Sn0_2$. After 12 hours of mixing and grinding, the samples were calcined at 850°C for 24 hrs in air. The samples were ground, sieved to obtain particles of ~640 mm in size and cold-pressed into a disc-shaped pellet of about 6 mm diameter and 1-2 mm thickness by applying a pressure of about 140 kN/cm^2. Finally, the samples were sintered in air under optimum conditions (Shaari *et al.* 1991) at 950°C for 24 hours.

The morphology of the materials thus prepared was observed by a scanning electron microscope model Joel JSM-35C. X-ray powder diffraction was done using Philips diffractometer PW 1730 and lattice constants of the compounds were determined. The Meissner effect, used as a litmus test for superconductivity, was observed by levitating a small strong permanent magnet, Nd-Fe-B, over liquid nitrogen-cooled samples.

Resistivity measurements on pure $YBa_2Cu_30_{7-\delta}$ were carried out by a standard d.c. four-probe method with a current of 1 mA. The superconducting transition temperature of a 5% Sn sample was also measured in terms of complex susceptibility, $\varkappa = \varkappa' - i\varkappa''$, using a Lakeshore a.c. susceptometer model 7000. Results of measurements for other samples will be reported in detail elsewhere.

RESULTS AND DISCUSSION

The X-ray powder diffraction patterns at various Sn concentrations are shown in *Fig. 1*. The diffraction patterns demonstrate that $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ exists almost as single phase materials for samples at x = 0.00, 0.01, 0.02 and 0.03 where the characteristic peaks of orthorhombic $YBa_2Cu_30_{7-\delta}$ predominate (Beyers and Shaw 1989). However for samples of x = 0.04, 0.05 and 0.06, other minor phases were observed and are evident from the additional peaks in the diffraction patterns.

Changes in the lattice constants of $YBa_2Cu_30_{7-\delta}$ against Sn concentrations are as shown in *Fig. 2*. The length of the b- and c-axes did not change drastically with the increase of Sn concentrations. On the other hand, the a-axis expanded significantly from Sn concentration of x = 0.03 and finally became equal to the b-axis at x ~ 0.06, the onset of transition from orthorhombic to tetragonal structure.

The effect of interstitial or lattice substitution of Sn is also evident from the volume expansion as shown in *Fig. 3*, where abrupt change in volume occurs at Sn concentration of x ~ 0.03. As yet there is no evidence as to whether Sn goes into the system interstitially or by lattice substitution and hence the ordering of Sn atoms is not known. However, Sn atoms do effect the system spatially.

More evidence for the onset of transition from orthorhombic to tetrago-

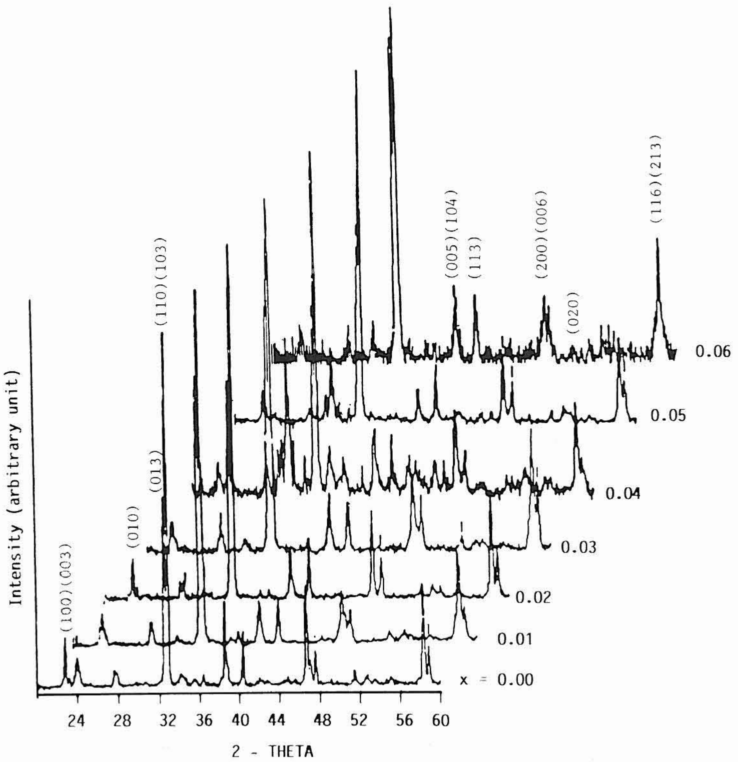

Fig 1. X-ray diffraction pattern of $(YBa_2Cu_3O_{7-\delta})_{1-x}(SnO_2)_x$ *(x = 0.00 to 0.06)*

nal phase is shown by the intensity peaks of the X-ray diffraction patterns at $2\theta \sim 32\text{-}33^o$ as shown in *Fig. 4.* As onset is approached, the minimum peak close to $2\theta \sim 32^o$ increases and finally almost equals the maximum peak. In order to observe the changing of the position of the minimum peak from $2\theta \sim 32^o$ to $2\theta \sim 33^o$, additional data for Sn concentration of $x \sim 0.07$ is required because at that concentration the system will exist completely in tetragonal phase. The evidence discussed above could similarly be seen from X-ray diffraction patterns at $2\theta \sim 38^o$ - 41^o , 46^o - 48^o and 58^o - 60^o, as these peaks represent the characteristic peaks of $YBa_2Cu_3O_{7-\delta}$ (Izumi *et al.* 1987).

Evidence of superconductivity in the system can be qualitatively deduced from the observation of shielding behaviour of the superconductors due to Meissner effect. In this work, all the samples (x = 0.00 to 0.06) displayed the behaviour well above liquid nitrogen temperature.

A previous finding (Beyers and Shaw 1989), suggests that T_c remains at 90K for oxygen concentration from $O_{7.0}$ to $O_{6.9}$, and then falls to a ~ 60K 'plateau' between $O_{6.7}$ and $O_{6.6}$ and finally drops to zero (i.e. not superconducting between $O_{6.5}$ and $O_{6.4}$) as shown in *Fig. 5.* Hence it could be deduced

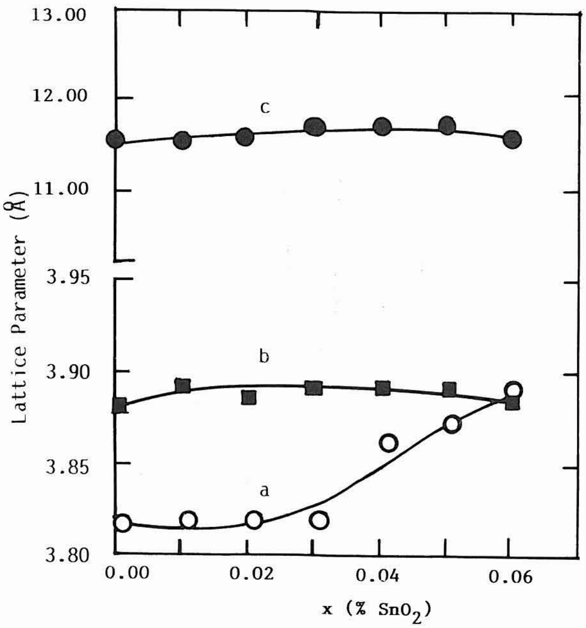

Fig. 2. *Dependence of lattice parameters upon x in* $(YBa_2Cu_3O_{7-\delta})_{1-x}(SnO_2)_x$

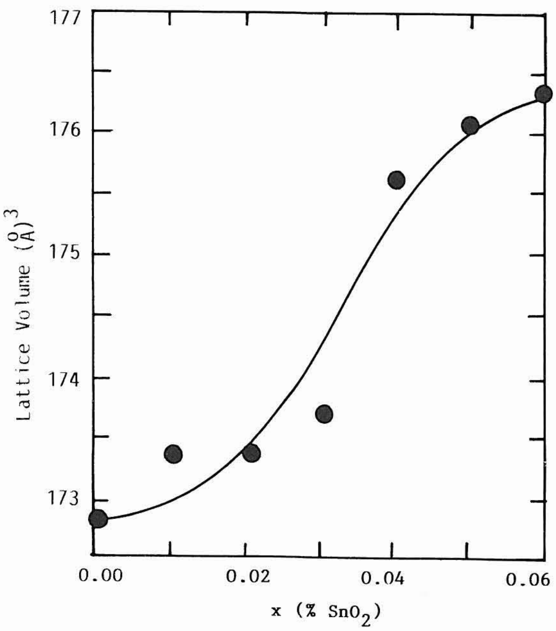

Fig. 3. Lattice volume of $(YBa_2Cu_3O_{7-\delta})_{1-x}(SnO_2)_x$

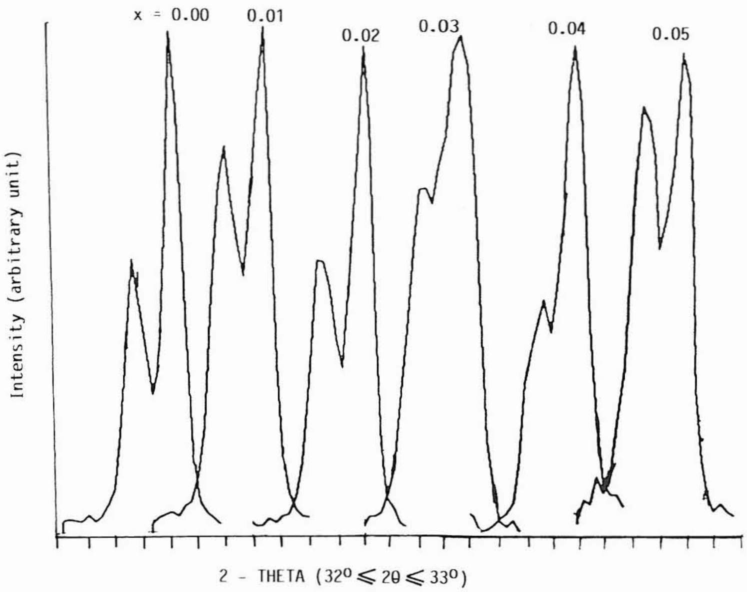

Fig. 4. Peak shifts of powder X-ray diffraction of $(YBa_2Cu_3O_{7-\delta})_{1-x}(SnO_2)_x$

that the oxygen content of the samples prepared in this work must be ~ $0_{6.8}$, since all samples displayed Meissner effect above 77K. Paulose *et. al.* (1991) suggested that the rate of oxygen absorption would increase in $YBa_2Cu_30_{7-\delta}$ by $Sn0_2$ addition.

A quantitative measurement of temperature dependence of sample resistance has been done. *Fig. 6* shows the temperature variation of resistance for pure $YBa_2Cu_30_{7-\delta}$ and T_c was found to be around 90K. From the qualitative measurements of the dependence of the component Π ' of the complex susceptibility with temperature for a 5% Sn sample, as shown in *Fig. 7*, T_c was found to be about 80K. More detailed results on the magnetic properties of the samples will be reported elsewhere.

CONCLUSION

In conclusion the substitution of Sn atoms up to 6 at% in the YBCO system does not give rise to a drastic change in T_c, which agrees with Suzuki *et al.* (1988), as compared to Zn, Fe or Co substitution (Strobed *et al.* 1988; Beyers and Shaw 1989; Shaari *et al.* 1992), where T_c is strongly suppressed. The retention of an orthorhombic structure with Sn atoms having little effect on T_c in the $(YBa_2Cu_30_{7-\delta})_{1-x}(Sn0_2)_x$ system up to x = 0.06 could be rationalized on the basis that Sn substitutes as +4 valence state (Zhang *et al.* 1989) and hence could draw excess oxygen into the structure in order to increase their oxygen coordination.

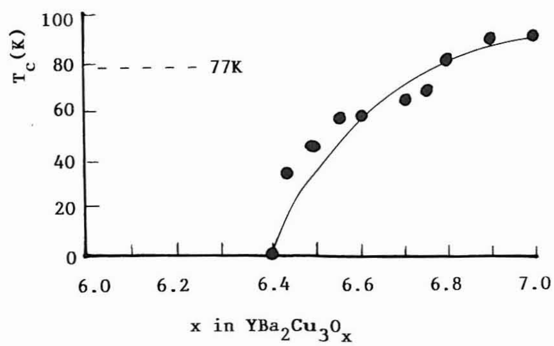

Fig. 5. Superconductivity transition temperature versus oxygen contents (Beyers and Shaw 1989)

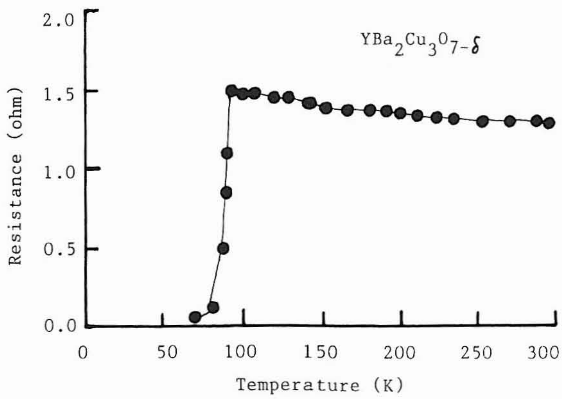

Fig. 6. Resistance versus temperature of pure YBaCuO

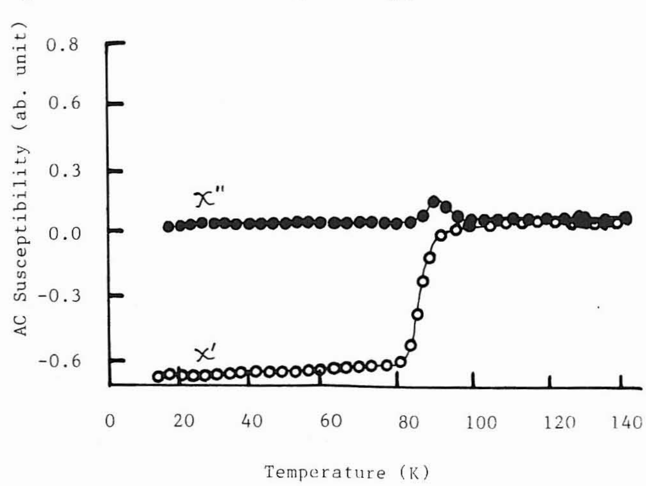

Fig. 7. Temperature variation of real X^1 and imaginary X^{11} components of susceptibility of (5% Sn)

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A. HALIM SHAARI, MANSOR HASHIM,
SIDEK HJ. AB. AZIZ, JAMIL SURADI
and NAEMAH MOHD. SHAFIE

Department of Physics
Faculty of Science and Environmental Studies
Universiti Pertanian Malaysia
43400 Serdang, Selangor Darul Ehsan, Malaysia

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