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SUPERCONDUCTIVITY STUDIES ON $(Y_{1-x}\ Ln_x)\ Ba_2Cu_3\ O_{7-\delta}$; Ln = La, Gd, Ho AND Tm

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Isostructural solid solutions of the type $(Y_{1-x}Ln_x)\ Ba_2Cu_3\ O_7$ (Ln = La, Gd, Ho and Tm) exhibit high T_c superconductivity (T_c = 90 - 95K) but Vegard's law is not obeyed. Compounds containing La are superconducting upto $x = 0.5$.

Key Words: High T_c Superconductivity; $Y\ Ba_2Cu_3\ O_7$; Solid Solutions

INTRODUCTION

EVER since the identification of $YBa_2Cu_3O_7$ as the single phase material responsible for high T_c superconductivity in the Y — Ba — Cu — O system with T_c = 91K,[1-4] several workers examined the T_c behaviour of chemically substituted isostructural phases at the Y, Ba, Cu and O— sites.[5-20] It is now known that $LnBa_2Cu_3O_7$, (*Ln* = rare earth other than La, Pr, Tb and Lu) also exhibit superconductivity with T_c = 88 - 93K, the value depending on *Ln*.[9]

The compound $YBa_2Cu_3O_7$, adopts the well-known perovskite (ABO_3) structure but has special crystal-chemical features: (*i*) The symmetry is orthorhombic with a tripled c-axis ($c \sim 3a_p$); (*ii*) The Y and Ba atoms have 8- and 10-fold oxygen coordination and unique sites; (*iii*) Two copper atoms exist as CuO— planar groups and one copper exists as ID-linked—O—Cu—O—Cu—chains; (*iv*) The structure tolerates appreciable oxygen deficiency: $YBa_2Cu_3O_{7-\delta}$, $0 \leqslant \delta \leqslant 0.8$ (Fig. 1).

The metallic behaviour and superconductivity in $YBa_2Cu_3O_7$ arise from the conduction band formed from the Cu-3d electrons. The T_c, however, is highly sensitive to δ; for δ = 0.05-0.2, T_c=91K; δ=0.2-0.4, $T_c \sim 60$K and for $\delta > 0.4$, no T_c is observed. Substitution at the Y site by a rare earth ion (*Ln*) retains the high T_c superconductivity, whereas substitution at the Ba site by Sr or Ca or substitution at the Cu site by other 3d- or 4d-transition element produces a decrease of T_c.[18-20] Substitution at the O-site by F or S has been tried[16,21,22] but the results have not been consistent nor reproducible.

$YBa_2Cu_3O_7$ has outstanding properties. Apart from being a special class of mixed oxide system, it exibits: (*i*) high T_c (zero resistance at and below (91K); (*ii*) very high critical magnetic field ($H_{c2} \sim 150$ Tesla, Type II superconductor); (*iii*)

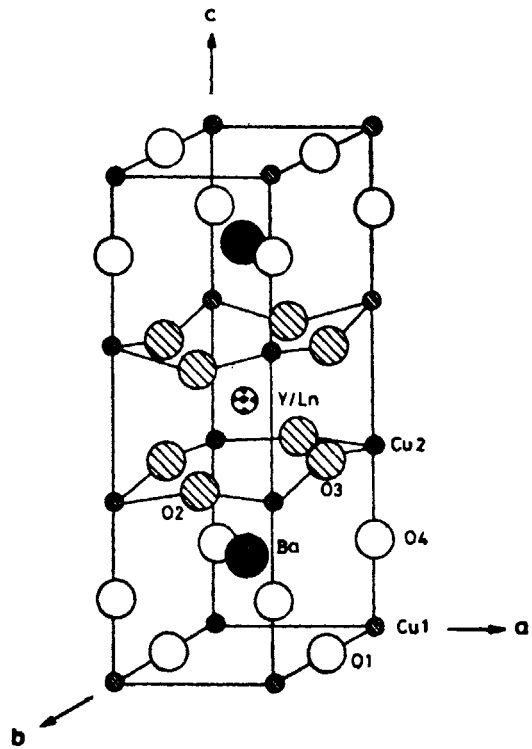

FIG 1 Structure of $Y/LnBa_2Cu_3O_7$.

P-type metallic behaviour (indicating holes as the majority charge carriers) and anisotropy in transport properties; and (*iv*) very short coherence length (~15–20Å). A good theory of high T_c superconductivity has to take cognizance of the above facts.[23,24]

Eventhough $LnBa_2Cu_3O_7$, *Ln* = Nd, Sm, Eu, Gd, Ho, Er, Tm and Yb exhibit high T_c similar to $YBa_2Cu_3O_7$ and these include *Ln*- ions with localised magnetic moments, subtle changes with respect to T_c, ρ_{300k} and ρ-T behaviour, and significant changes in H_{c2}, J_c (critical current) and related properties are expected when the lanthanide ion is varied. In fact H_{c2} and J_c improvements have been reported recently in *Ln*-doped $YBa_2Cu_3O_7$.[25,26] Presently the authors report on the synthesis and superconductivity behaviour of $(Y_{1-x}Ln_x)\ Ba_2Cu_3O_7$, *Ln* = La, Gd, Ho and Tm; $0 \leqslant x \leqslant 1.0$.

EXPERIMENTAL

The compounds $(Y_{1-x}Ln_x)\ Ba_2Cu_3O_7$, *Ln* = La, Gd, Ho and Tm and $x = 0.0$ to 1.0 in steps of 0.2 were prepared fromstoichiometric amounts by the high temperature solid state reaction. High purity starting materials were employed: Ln_2O_3, *Ln* = La, Gd, *Y* (Indian rare earths, 99.91%); Ln = Ho and Tm (Cerac UK,

99.9%), $BaCO_3$ (BDH AR, 99.5%) and CuO (Prepared from Cu powder, 99.9% by the decomposition of nitrate). A uniform heating procedure was adopted for the synthesis; powders thoroughly mixed with acetone in an agate mortar and pestle, and heated in Pt crucible 950 °C, 24th, air, two repeat grindings and heatings, pelletization, heating at 950 °C, 24h, air, and final heating at 900 °C, 24 h; flowing O_2; cool to 600 °C; 24h; flowing O_2, and slow cool to room temperature in O_2. One significant point is that the synthesis has to be done under dry mixing conditions; wet (water) mixing after the first heating schedule drastically affects the superconducting properties of the samples. The samples were characterised by powder X-ray diffraction (XRD) (Philips PW-1140, Ni filter; CuKα radiation; 40kV; 20mA).

Four probe d.c. electrical resistivity (ρ) measurements were carried out in the range 77–300 K on sintered, oxygen-annealed pellets (8mm dia; 2–3mm thick) with ultrasonically-soldered (Fibra-sonics; Inc., USA) indium metal contacts. T_c was taken as the temperature at which zero resistance was noted (Tc^{zero}). The Tc^{onset} values are those at which ρ dropped significantly from the normal (nearly linear) high-temperature behaviour. The transition width (ΔT_c) is the temperature difference corresponding to 90% and 10% of the drop in resistivity values during the superconductivity transition.[27] T_c^{zero} values are accurate to $\pm$ 0.5 K. Negligible hysterisis was noted in heating and cooling cycle ρ-T plots. An inductance bridge with carrier frequency amplifier test set-up consisting of two coils of 50μm dia copper wire of 4000 turns each, dipped in liq. N_2 with the test sample, was used to quickly check the samples for superconductivity at and above 77K (coil test).[28] A positive deflection is indicative of Meissner effect (flux expulsion). Detailed ac magnetic susceptibility measurements were carried out using an apparatus described previously.[29] A small field of 10G was applied. The Seebeck coefficient has been measured in the range 77–300 K with respect to copper metal and the apparatus has been described elsewhere.[30]

Results and Discussion

$(Y_{1-x}Ln_x)\ Ba_2Cu_3O_7$, *Ln* = Gd, Ho *and* Tm *System*

XRD patterns show that the isostructural series of solid solutions with the orthorhombically-distorted perovskite structure is formed in all cases. Sharp XRD lines were noted in all $Y_{1-x}Ln_x$ series for $0 \leqslant x \leqslant 0.4$ indicating good crystallinity of the materials and ordering of the ions in the lattice. The δ values in $(Y_{1-x}Ln_x\ Ba_2Cu_3O_{7-\delta}$ have been estimated to be around 0.1 to 0.2 in all the compounds (iodimetry). All the phases exhibit high T_c superconductivity (coil test, positive $T_c > 77$K). However, our results show that T_c^{onset} and T_c^{zero} values do not obey Vegard's law behaviour for various x. Some compositions exhibit T_c^{zero} as high as 94 K (Fig. 2). We also find that ρ300K values for the solid solutions are lower (< 1m Ω cm) than the pure $LnBa_2Cu_3O_7$, *Ln* = Gd, Ho, Tm and *Y* (typically 1-3 m Ω cm). The T_c values obtained by resistivity studies agree well with those obtained from ac susceptibility method.

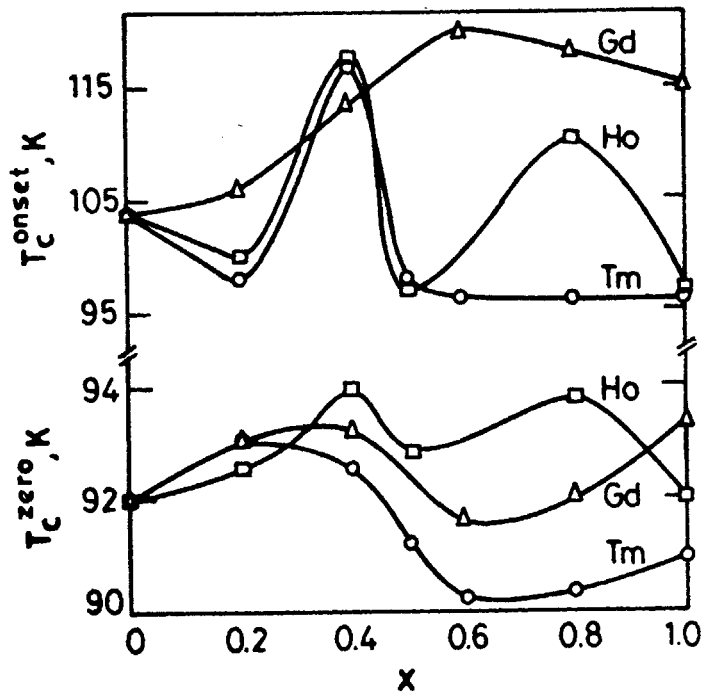

FIG 2 T_c^{onset} and T_c^{zero} *vs* x plot in $Y_{1-x}Ln_xBa_2Cu_3O_7$ (Ln = Gd, Ho and Tm)

Seebeck coefficients (α) have been measured on pure $YBa_2Cu_3O_7$ and representative solid solution compositions. The values are small ($\sim$2–5μV/K) and positive indicating that the majority charge carriers are holes in all these high T_c superconductors. This situation can arise due to conduction in a more than half-filled Cu 3d band or due to the overlapping conduction bands formed from the Cu 3d-02p bands. The Seebeck coefficients drop to zero at T_c as expected of a bulk superconductor. The α-T behaviour is more or less linear in the range 150–300 K but shows an anamolous enhancement in the range (T_c^{zero}—150K). This behaviour is encountered in pure $YBa_2Cu_3O_7$ and the solid solutions presently studied.

$(Y_{1-x}La_x)\ Ba_2Cu_3O_7$, $0 \leqslant x \leqslant 1.0$ *System*

XRD Patterns show that solid solutions are formed in the $(Y_{1-x}La_xBa_2Cu_3O_7$, $0 \leqslant x \leqslant 1.0$ series with the perovskite structure. While $YBa_2Cu_3O_7$ is orthorhombic, $LaBa_2Cu_3O_7$ shows a tetragonal structure ($a = b$), in good agreement with the data reported in the literature.[8] In the solid solutions, the orthorhombic structure is retained upto $x = 0.5$–0.6 and tetragonal phase is stabilized for $x >$ 0.6. This has been clearly established by the merging of XRD peaks corresponding to *hkl* (103, 013), (020, 200) and (123, 213).

Preliminary studies (coil test) indicated that the phases with $0 \leqslant x \leqslant 0.5$ are superconducting above 77 K. Pure $LaBa_2Cu_3O_7$ and phases with $x > 0.5$ did

not show superconductivity above 77 K. Detailed studies are yet to be made. It may be pointed out that Kitazawa[31] reported that superconductivity above 70 K (and orthorhombic distortion) can be induced in pure $LaBa_2Cu_3O_7$ by annealing it in O_2 at 300–350 °C for 3–5 days. Annealing studies on $LaBa_2Cu_3O_7$ and solid solutions with $x > 0.5$ are presently underway and the results will be reported elsewhere.

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