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## Freeze dry synthesis and micro-structural properties of optimally Ir-(III) doped-GdBCO semiconducting material

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### ABSTRACT

The semiconducting sample with formula  $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$  was synthesized by using solution route technique to get maximum homogeneity inside the bulk of the material. Structural and microstructural properties were monitored by using both of XRD and SEM evaluating that gadolinium-based cuprate has the semiconducting tetragonal phase as proved in the X-ray diffractogram, grain size of the material bulk was found to be in between 0.23-0.72 $\mu$ m. Magnetic measurements indicated that the Ir-doped gadolinium cuprate system exhibits an semiconducting behavior confirming that iridium hole dopings enhance the semi-conduction mechanism of the tetragonal cuprates.

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### KEYWORDS

Solution route synthesis;  
X-ray diffraction;  
SE-microscopy;  
Semiconductors;  
Magnetic properties.

### INTRODUCTION

123-HTc- layered cuprates superconducting regime is considered the most interesting superconducting materials for various reasons, in particular for their rather high critical temperature  $T_c$  and high critical current density  $J_c$ . Many researchers have investigated the effect of metal cation dopants on the 123-YBCO superconducting system<sup>[1-8]</sup>. Others like<sup>[9]</sup> have studied the effect of  $CeO_2$  and  $PtO_4$  mixed oxide additives on the microstructural and critical current density  $J_c$ . They reported that (Ce + Pt) oxides added to the melt-textured YBCO have significantly improved on the value of  $J_c$   $4.3 \times 10^4$  A/cm<sup>2</sup>. The role of additives as impurity phases like (silver, silver oxide,.) to improve processing, magnetization and microstructure of YBCO system were studied by many authors<sup>[10-16]</sup>.

Since the discovery of high- $T_c$  superconductivity<sup>[17]</sup>,

there has been an explosion of experimental and theoretical studies on these materials.

A large number of these studies are restricted to the effects of substitution of rare earth (R) elements for Y that is mostly helpful in understanding the superconducting properties and their dependences on different parameters. Among various isomorphic substitutions possible in  $YBa_2Cu_3O_{7-\delta}$ , the substitution of Pr<sup>[18-20]</sup>, (Ce)<sup>[21,22]</sup>, and Tb<sup>[23-25]</sup>, for Y have received the most attention. The reason for this interest is that these substitutions suppress the transition temperature of superconductivity drastically. The major goal in the present article is to investigate the effect of solution route synthesis on;

- Structural and micro-structural properties of Ir-doped GdBCO sample.
- Magnetic properties of optimally Ir-doped GdBCO sample.

## EXPERIMENTAL

### Samples preparation

The best iridium containing composite with general formula;

$Gd_{1-x}Ir_xBa_2Cu_3O_z$ , where  $x = 0.3$  mole was selected from another study for authors to be the target of this investigation. The preparation was attempted by the freeze dry route and sintering procedure using the molar ratios of  $Ir_2O_3$ ,  $Gd_2O_3$ ,  $BaCO_3$  and  $CuO$  each of highly pure chemical grade purity. The mixtures were ground carefully then solublize in few drops of concentrated nitric acid forming nitrate extract which diluted by distill water. The nitrate solution was neutralized by using 30 % urea solution then forwarded into liquid nitrogen dishes under vacuum for 2 hrs inside freeze dry machine see figure 1.

The freeze product was forwarded to muffle furnace and calcinations process was performed at  $800^\circ C$  under a compressed  $O_2$  atmosphere for 16 hrs then reground and pressed into pellets (thickness 0.2 cm and diameter 1.2 cm) under 5 Ton/cm<sup>2</sup>. Sintering was carried out under oxygen stream at  $920^\circ C$  for 70 hrs. The samples were slowly cooled down ( $20^\circ C/hr$ ) till  $550^\circ C$  and annealed there for 10 hrs under oxygen stream. The furnace is shut off and cooled slowly down to room temperature. Finally the materials are kept in vacuum desiccator over silica gel dryer.

### Phase identification

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using  $Cu-K\alpha$  radiation source, Ni-filter and a computerized STOE diffractometer/Germany with two theta step scan technique.

Scannig Electron Microscopy (SEM) measurements were carried out at different sectors in the prepared samples by using a computerized SEM camera with elemental analyzer unit (PHILIPS-XL 30 ESEM/USA).

### Magnetic measurements

The cryogenic AC-susceptibility of the prepared materials was undertaken as a function of temperature recorded in the cryogenic temperature zone down to 30 K using liquid helium refrigerator.

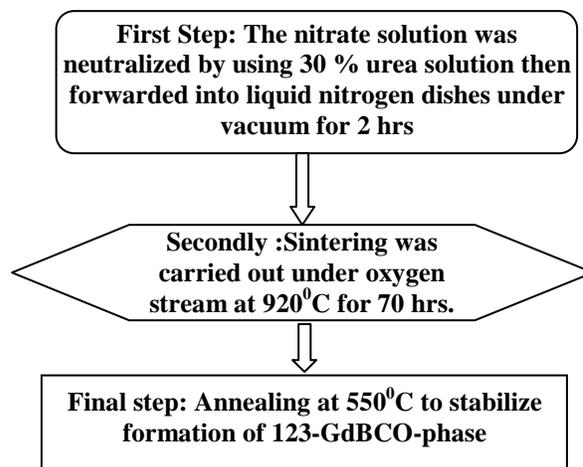


Figure 1: Flowchart diagram of Ir-doped GdBCO synthesis

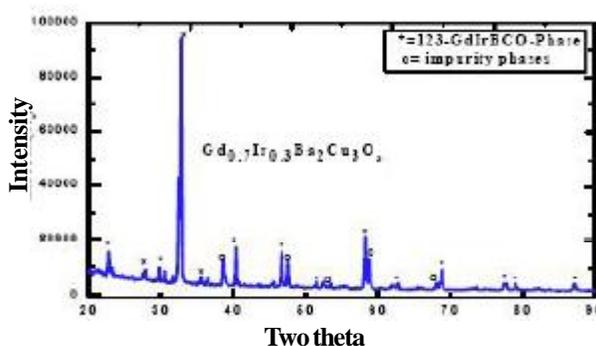


Figure 2: X-ray diffractogram recorded for  $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$  sample synthesized by freeze dry route

## RESULTS AND DISCUSSION

### 1. Phase identification

Figure 2 displays the X-ray powder diffractometry pattern for optimally Ir-doped GdBCO ( $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$ ). Analysis of the corresponding  $2\theta$  values and the interplanar spacings  $d$  (Å) were carried out and indicated that, the X-ray crystalline structure mainly belongs to a single non-superconductive tetragonal phase 123-GdBCO in major besides few peaks of  $Ir_2O_3$  as secondary phase in minor. It is well known that;

Superconductive 123-orthorhombic  $\leftrightarrow$  semi conductive phase 123-tetragonal and hence iridium makes a shift in structure towards tetragonal phase.

The unit cell dimensions were calculated using the most intense X-ray reflection peaks to be  $a = 3.8271$  Å,  $b = 3.8271$  Å and  $c = 11.6431$  Å for the optimally

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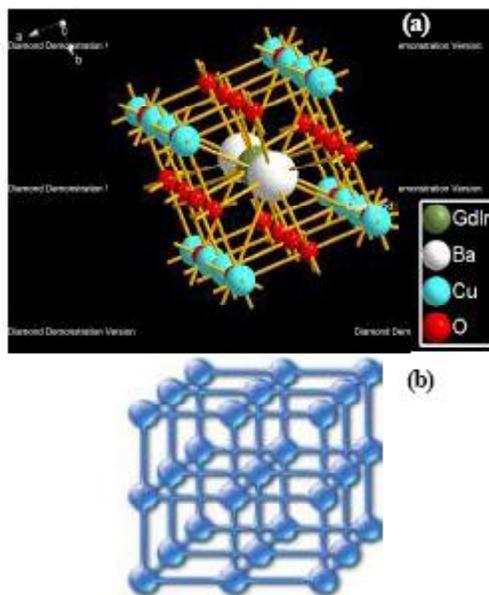


Figure 2: (a): 123-tetragonal phase of  $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$ ; (b) : Cubic crystal structure of iridium ion

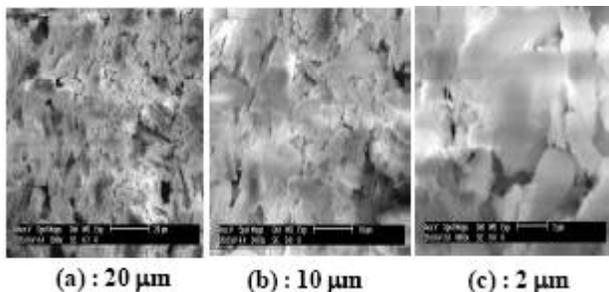


Figure 3 (a-c): SEM-micrographs recorded for optimally Ir-doped GdBCO ( $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$ ) with three different magnification factors; (a) : 20  $\mu m$  (b) : 10  $\mu m$  and (c) : 2  $\mu m$

TABLE 1

Element	123-LBCO Wt %	123-GdBCO At %	K-Ratio	Z	A	F
O K	15.88	51.25	0.1029	1.1394	0.1431	1.0014
CuK	5.29	30.13	0.0379	1.1733	0.9253	1.0031
BaK	18.22	19.48	0.1931	1.0746	0.9907	1.0213
Ir L	18.96	2.65	0.0513	0.6181	1.0418	1.0198
GdL	19.68	6.98	0.1364	0.6175	1.0101	1.0211

Ir-doped 123-GdBCO phase which is fully agreement with those mentioned in the literature<sup>[4-8]</sup>.

It is obviously that, the additions of  $Ir_2O_3$  has a negligible effect on the main crystalline structure 123-GdBCO with Ir-content ( $x = 0.3$ ) as shown in figure 2.

From figures 2(a,b) one can indicate that 123-tetragonal phase (Figure 2a) is the dominating phase by

ratio exceeds than 90% confirming that Ir-ion which has cubic lattice see figure 2b substitutes successfully on the Gd-sites without damaging the original non-superconducting tetragonal-phase.

TABLE 1 explains EDX-elemental analysis data recorded for  $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$  that prepared via freeze dry route. It is clear that the atomic percentage recorded is approximately typical with the molar ratios of the prepared sample emphasizing the quality of preparation through freeze dry technique.

On the basis of ionic radius Ir-ion can substitute on the Gd-sites causing slight shrinkage in the lattice without destroying it as clearly appears in the x-ray diffractogram figure 2. since 123-tetragonal phase is clearly assigned in our x-ray patterns by \* as shown in figure 2.

## 2. SE-microscopy measurements

Figure (3a-c) show the SEM-micrographs recorded for optimally Ir-doped GdBCO ( $Gd_{0.7}Ir_{0.3}Ba_2Cu_3O_z$ ). The estimated average of grain size was calculated and found in between 0.23-0.72  $\mu m$  supporting the data reported in<sup>[27]</sup>.

The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline Ir-doped-GdBCO sample, such that the differences in the molar ratios EDX estimated for the same sample is emphasized and an evidence for the existence of 123-GdBCO tetragonal phase with good approximate to molar ratios.

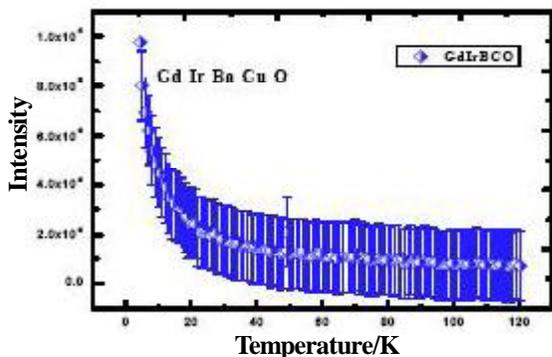
From figure (3a-c), it is so difficult to observe inhomogeneity within the micrograph due to that the powders used are very fine and the particle size estimated is too small.

The grain size for Ir-doped 123-GdBCO-phase was calculated according to; Scherrer's formula<sup>[28]</sup>,

$$B = 0.87 \lambda / D \cos \theta \quad (1)$$

where D is the crystalline grain size in nm,  $\theta$ , half of the diffraction angle in degree,  $\lambda$  is the wavelength of Xray source (Cu-K $\alpha$ ) in nm, and B, degree of widening of diffraction peak which is equal to the difference of full width at half maximum (FWHM) of the peak at the same diffraction angle between the measured sample and standard one.

From SEM-mapping, the estimated average grain size was found to be (1.21-1.54 $\mu m$ ) which is relatively large in comparison with that calculated applying



**Figure 4 :** Magnetic susceptibility curve recorded as a function of absolute temperatures for tetragonal-Gd<sub>0.7</sub>Ir<sub>0.3</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>z</sub> sample synthesized via freeze dry route

Scherrer's formula for pure 123-phase ( $D \sim 0.67 \mu\text{m}$ ). This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology. Furthermore, in our EDX (energy disperse X-ray) analysis, Ir<sup>3+</sup> was detected qualitatively with good approximate to the actual molar ratio but not observed at 123-GdBCO grain boundaries which confirm that, iridium (III) has diffused regularly into material bulk of superconducting 123-GdBCO-phase and Ir-ion induces in the crystalline structure through solid state reaction by some extent. The inclusion of Ir-ion is confirmed also by the enhancing the semiconducting behavior of tetragonal GdBCO semiconductor.

### 3. Magnetic and electrical properties

Figure 4 exhibits magnetic susceptibility curve recorded as a function of absolute temperatures for tetragonal-Gd<sub>0.7</sub>Ir<sub>0.3</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>z</sub> sample synthesized via freeze dry route. It is clear that the conduction increases as temperatures raise reflecting semiconductor behavior for IrGdBCO sample. Although the iridium dopant has metallic behavior with electrical resistivity ( $4.7 \times 10^{-8} \text{ohm.m}$ ) as reported in literatures<sup>[29-32]</sup> it enhances semiconduction mechanism inside material bulk of GdBCO.

Generally it is well known that the conduction in the cuprates depend upon Cu<sub>2</sub>O and CuO chains which are known as p-type semiconductors exhibiting narrow band gaps.

For example, Cu<sub>2</sub>O has a direct band gap (2.0 eV), which makes it a promising material for the conversion of solar energy into electrical and chemical energy[33].

From this point of view iridium as dopant element with metallic character expected to make a shift towards semiconducting behavior as achieved in our investigation.

## COCLUSIONS

The conclusive remarks inside this article can be summarized as the follow ;

1. Freeze dry technique exhibits structure quality as preparation technique.
2. Ir-dopant make a shift towards tetragonal phase.
3. SE-micrographs confirmed that Ir-ions distribute regularly through out the lattice structure of GdBCO without destroying 123-phase.
4. Magnetic order of GdBCO changed to non-superconductive order semiconducting order as result of iridium doping.

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