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Sol-gel synthesis for optimally doped-germanium (III)-NdBCO superconducing material

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ABSTRACT

The superconducting sample with formula $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ was synthesized by using sol-gel route with two different solution precursors depending upon metals-citerates complexed with ethylenediamine. Structural and microstructural properties were monitoring by using both of XRD and SEM evaluating that neodymium-based cuprate has the superconducting 123-orthorhombic phase as proved in the X-ray diffractogram,grain size of the material bulk was found to be in between 0.31-0.82 μ m.Magnetic measurements indicated that the Ge-doped neodymium cuprate system exhibits an superconducting behavior(Tc-offset = 92.1K) confirming that semi-conducting germanium dopings enhance the conduction mechanism of the superconducting sample.

KEYWORDS

Sol-Gel synthesis;
X-ray diffraction;
SE-microscopy;
Superconductors;
Magnetic properties.

INTRODUCTION

Many researchers have investigated the effect of metal cation dopants on the123-YBCO superconducting system[1-8].Others like[9] have studied the effect of CeO_2 and PtO_4 mixed oxide additives on the microstructural and critical current density Jc.They reported that (Ce + Pt) oxides added to the melt- textured YBCO have significantly improved on the value of Jc.The role of additives as impurity phases like (silver, silver oxide,TiO_2,V_2O_3,..) to improve processing, magnetization and microstructure of YBCO system were studied by many authors[10-16].

Since the discovery of high-T_c superconductivity[17], there has been an explosion of experimental and theoretical studies on these materials.

A large number of these studies[18-25] 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.

The reason for this interest is that these substitutions suppress the transition temperature of superconductivity drastically.

Wet chemistry, and particularly sol-gel processing is one of the most promising way to get an excellent homogenization at an atomic scale of the elements and a high reactivity of the precursors. This was developed by Kakihana et al. to prepare high Tc cuprates such as Y-123, Y-124, Bi-2212 and Bi-2223 phases[26].

The major goal in the present article is to investigate the effect of sol-gel synthesis on;

a. Structural and micro-structural properties of Ge-doped NdBCO sample.
b. Magnetic properties of optimally Ge-doped NdBCO sample.

EXPERIMENTAL

A. Samples preparation

The best optimally-doped- germanium containing composite with general formula; $Nd_{1-x}Ge_xBa_2Cu_3O_z$, where x = 0.2 mole was selected from another study for authors to be the target of this investigation.

Sol-gel technique was applied as high quality technique yielding to maximum homogeneity inside material bulk. This route is based on the formation of a precursors which are prepared through polyesterfication between metal-citrate complexes and ethylene glycol.

The formation of sol-gel product was attempted by mixing two different precursors together at final stage. First precursor is forming from molar ratios of both of Nd_2O_3 and Ge_2O_3 which initially dissolved in few drops of nitric acid forming nitrates solution that neutralized by 25 % urea solution (pH~6.5). Second precursor is forming from barium and copper nitrates solutions that mixed by molar ratios in the main molecular formula Ba :Cu = 2 : 3 and the pH was adjusted to be ~6. The second stage of preparation the solutions of two precursors were mixed together in one beaker which heated at 110^{0}C then ethylene glycol was added carefully until sol-gel with heavy nature is obtained.

The product was forwarded firstly to dryer oven at 200^{0}C for two hours then to the muffle furnace. The calcinations process was performed at 800^{0}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^2. Sintering was carried out under oxygen stream at 920^{0}C for 30 hrs.The samples were slowly cooled down (20^{0}C /hr) till 550^{0}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.

B. Phase identification

The X-ray diffraction (XRD) measurements were carried out at room temperature on the fine ground samples using Cu-Kα 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).

C. 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 by using quantum interference device magnetometer. The field was kept at H = 4 Oe throughout the measurement. The measured magnetic moment (emu) was divided by the weight of the sample to yield mass magnetization, M (emu/g) which was plotted as a function of temperature.

RESULTS AND DISCUSSION

I. Phase identification

Figure 1 displays the X-ray powder diffractometry pattern for optimally Ge-doped NdBCO ($Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$). Analysis of the corresponding 2θ values and the interplanar spacings d (Å) were carried out and indicated that,the X-ray crystalline structure mainly belongs to a single superconductive orthrohmbic phase 123-NdBCO in major. It is well known that ;

Superconductive 123-orthohombic↔semiconductive phase 123-tetragonal and hence germanium (III) dopant makes a shift in structure towards orthrohmbic phase.

The unit cell dimensions were calculated using the most intense X-ray reflection peaks to be a = 3.8137 Å, b = 3.8371Å and c = 11.6431Å for the optimally Ge-doped 123-NdBCO phase which is fully agreement with those mentioned in the literature[4-8].

It is obviously that, the additions of Ge(III) has a negligible effect on the main crystalline structure 123-NdBCO with Ge-content (x = 0.2) as shown in figure 1 which reflect the suitability of both charge and atomic radii fitting in between Nd and Ge ion.

TABLE 1 explains EDX-elemental analysis data recorded for $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ that prepared via Sol-Gel 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 Sol-Gel technique.

On the basis of ionic radius Ge-ion can substitute on the Nd-sites causing slight shrinkage in the lattice without destroying it as clearly appears in the x-ray diffractogram figure 1.

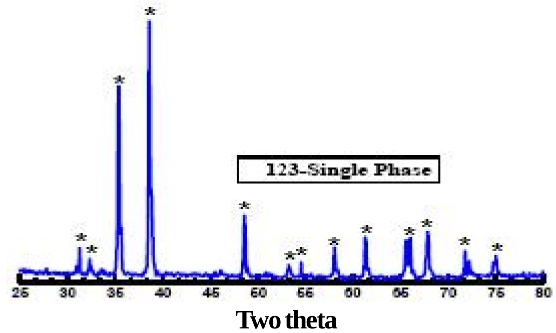

Figure 1: X-ray diffraction pattern recorded for optimally Ge-doped $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ superconductor

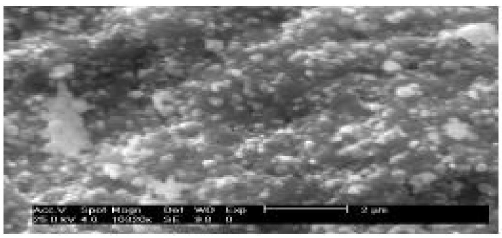

Figure 2 : SE-Micrograph recorded for 123- $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ superconductor with magnification factor = 2 μm

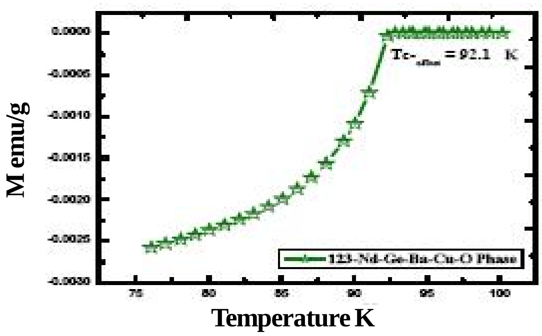

Figure 3: Magnetic susceptibility curve recorded for $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ HTc-ceramic superconductor

II. SE-microscopy measurements

Figure 2 show the SEM-micrograph recorded for optimally Ge-doped NdBCO

$Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$. The estimated average of grain size was calculated and found in between 0.31-0.82μm supporting those data reported in[27].

The EDX examinations for random spots in the same sample confirmed and are consistent with our XRD analysis for polycrystalline Ge-doped -NdBCO 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-NdBCO orthorhombic superconductive phase.

TABLE 1 : EDX-elemental analysis recorded for 123-Ge-doped-NdBCO system

123-NdGeBCO Element	123-NdGeBCO Wt %	At %	K-Ratio	Z	A	F
O K	15.88	54.25	0.1089	1.1794	0.1431	1.0024
CuK	5.29	29.83	0.0279	1.1133	0.9113	1.0051
BaK	18.22	18.98	0.1735	1.0733	0.9907	1.0013
Ge L	18.96	2.19	0.0499	0.6131	1.0398	1.0188
NdL	19.68	7.76	0.1239	0.6111	1.0121	1.0231

From figure 2, it is so difficult to observe inhomo geneitiy within the micrograph due to that the quality of sol-gel preparation technique.

The grain size for Ge-doped 123-NdBCO-phase was calculated according to;

Scherrer's formula[28], $B = 0.87\,\lambda/D\cos\theta$ **(1)**

where D is the crystalline grain size in nm, θ,half of the diffraction angle in degree, λ is the wavelength of X-ray source (Cu-Kα) 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-maping, the estimated average grain size was found to be (0.31-0.82μm) which is relatively small in comparison with that calculated applying Scherrer's formula for pure 123-phase (D~0.89μm).

This indicates that, the actual grain size in the material bulk is smaller than that detected on the surface morphology depending upon the homogenization dgree inside material bulk which is function in the preparation technique.

These results confirm that, Ge (III) has diffused regularly into material bulk of superconducting 123-NdBCO-phase and Ge-ion induces in the crystalline structure through solid state reaction reflecting the quality of preparation by using sol-gel route[26].

III. Magnetic and electrical properties

Figure 3 exhibits magnetic susceptibility curve recorded as a function of absolute temperatures for orthorhombic - $Nd_{0.8}Ge_{0.2}Ba_2Cu_3O_z$ sample synthesized via sol-gel route.It is clear that the Tc-offset = 92.1 K is typical to those reported in literatures[29-33] reflecting superconducting behavior for NdGeBCO sample. Although the germanium dopant has semi-conducting behavior it enhances superconduction mechanism inside material bulk of NdBCO.

Generally it is well known that the conduction in the cuprates depend upon Cu_2O and CuO chains which are known as p-type semiconductors exhibiting narrow band gaps. For example, Cu_2O 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[34].

From this point of view logically germanium as dopant element with metallic character expected to make a shift towards semi-conducting behavior which is not achieve in our investigations.

COCLUSIONS

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

1. Sol-gel technique exhibits structure quality as preparation technique.
2. germanium-dopant make a shift towards superconductive orthorhombic phase.
3. SE-micrograph confirmed that Ge-ions distribute regularly through out the lattice structure of NdBCO without destroying 123-phase.
4. Magnetic order of NdBCO still as it is without change (superconductive diamagnetic order).

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