

# New Phases of YBaCuGeO Superconductors Identified from X-ray Diffraction and Infra-red Absorption Measurements

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## Abstract

X-ray powder diffraction patterns and infra-red absorption spectra have been evaluated and analysed for the  $Y_1Ba_2Cu_3O_{7-\delta} - Ge_x$  compound samples prepared by the solid state reaction with  $x$  values ranging from 0.0 to 1.13. All samples show bulk superconductivity above liquid nitrogen temperature using the levitation test (Meissner effect). Samples with Ge content up to  $x = 0.2$  have offset  $T_c$  between 83K and 92K while the sample with  $x = 1.13$  shows semiconducting behavior above 100K. As a result of the solid state interaction between YBCO and Ge, new phases are observed and determined, mainly three phases are concluded from X-ray powder diffraction analysis: (i) Ba<sub>2</sub>GeO<sub>4</sub> (ii) Y<sub>2</sub>BaCuO<sub>5</sub> (iii) BaCO<sub>3</sub>. The unit cell parameters  $a$ ,  $b$  and  $c$  of the orthorhombic superconducting phase are calculated for all the prepared samples. The anisotropy factor is evaluated and related to the new structural phases in YBCO-Ge composite system.

The I-R absorption spectra for the samples with orthorhombic symmetry have been determined. The phonon modes between  $\sim 400\text{ cm}^{-1}$  and  $630\text{ cm}^{-1}$  are attributed to the  $Cu - O$  octahedron and pyramid vibrations for the  $CuO_2$ -planes and CuO-chains, while the peaks in the range from  $\sim 700\text{ cm}^{-1}$  to  $\sim 860\text{ cm}^{-1}$  may be due to defects such as the new phase Ba<sub>2</sub>GeO<sub>4</sub> and the green phase Y<sub>2</sub>BaCuO<sub>5</sub>. The obtained results are discussed according to the superconductor - semi-conductor composite model and with the phonon-mediated charge transfer between  $CuO_2$ -planes and CuO- chains through apex oxygen (BaO).

**Key Words:** Superconductors, X-ray, Infra-red, YBCO, Ge.

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## 1. Introduction

An important problem encountered in the study of the possible applications of high- $T_c$  superconductors in electronics is the superconductor - semiconductor contact, i.e. selection of such pairs of materials whose elements of the composition would have the smallest effect on each others properties.

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In particular, the doping of a superconductor by the atoms of a semiconductor should not degrade the characteristics of the superconductor. There is therefore the need to study the properties of a superconductor doped with semiconductor elements.

The superconducting properties of high-  $T_c$  superconductors are known to be degraded for YBCO 1-2-3 system doped with various elements (except for Ag and Au) [1]. At the same time, a partial substitution by lead for bismuth in a 2-2-2-3 Bi-system stabilizes the superconducting phase transition near  $T_c = 108-110 K$  [1], rendering it a more abrupt transition.

Since lead is an element of the fourth group, it would be of interest to study the effect of doping with semiconductor elements of the same group, in particular doping with Ge produces a new superconducting phase transition at  $T_c = 130 K$  in the  $Bi_{1.64}Pb_{0.36}Sr_2Ca_2Cu_{3-y}Ge_yO_{10}$  system [2].

The interaction between YBCO and Ge with mole ratio of 1:1 was recorded for only one sample by the Japanese group [3]. Their results indicated that Ge destroyed the superconducting phase.

In this study, we report the crystallographic parameters of YBCO-Ge composite system and separate the new structural phases due to semiconductor superconductor interaction by X-ray powder diffraction patterns and I-R absorption spectra, to clarify the nature of interaction towards possible high performance superconductor applications. Among these applications is the preparation of high- $T_c$  superconductors as YBCO thin films deposited directly on semiconductors as Ge, for electronic usage incorporating the best of what superconductors and semiconductors have to offer in new devices [4-6].

## 2. Experimental

### 2.1. Samples preparation

The YBCO-Ge powders were synthesized following the conventional ceramic route. High purity  $Y_2O_3$ ,  $BaCO_3$ , CuO and Ge (Aldrich) were mixed in molar ratio 1 : 2 : 3 :  $Ge_x$  ( $x = 0$  to 1.13) and calcined in an alumina crucible firstly at  $900^\circ C$  for 24 hr, secondly at  $920^\circ C$  for 60 hr, then ground, pressed into pellets and finally treated by a heat cycle from  $920^\circ C$  to room temperature with oxygen flow to get the orthorhombic structure of YBCO-Ge composite system.

### 2.2. D. C. resistance

The D. C. resistance was measured by the standard four-probe method. The constant current source model YOKOGAWA 7651 was used. The voltage drop was measured by a nano-voltmeter type Keithely model 181 and the temperature was recorded with a calibrated platinum resistance Pt-100 attached to a Keithely DMM model 196.

### 2.3. X-ray powder diffraction

X-ray powder diffraction is used for crystal structure determination of the prepared samples by using X'pert type Philips diffractometer 2000 with wavelength of  $Cu - K_\alpha 1 (\lambda = 1.54056 \text{ \AA})$ .

### 2.4. Infra-red measurements

The infra-red absorption spectra were recorded at normal incidence of light in the range from 200 to  $1000 \text{ cm}^{-1}$  by ATI Mattson Genesis I IR-Spectrometer. A small amount of each sample was mixed with KBr powder and pressed into pellets of 13 mm diameter for IR absorption measurements.

### 3. Results and Discussion

#### 3.1. Resistance versus temperature results

A levitation test (Meissner effect) carried out on all the prepared samples of the YBCO-Ge composite system shows bulk superconductivity above liquid nitrogen temperature. Samples with Ge content up to  $x = 0.2$  show metallic behavior of resistance at temperatures higher than the transition temperature  $T_c$ .

The offset  $T_c$  decreases from 92 K to 83 K with the Ge content ranging from  $x = 0$  to  $x = 0.12$ , then increases from 86 K for Ge content  $x = 0.15$  to 92 K for  $x = 0.2$  as listed in Table 1 [7].

The sample with  $x = 1.13$  shows a semiconducting behavior at temperatures higher than 100 K, then a sudden fall in resistance is observed at  $T \approx 100$  K, but did not reach zero till  $T = 77$  K [7] which suggests the existence of a  $T_c$  value less than 77 K. The detection of such  $T_c$  value requires either a different cooling technique to reach temperature lower than liquid nitrogen, or a non-contact inductive method to reveal the superconductivity of the isolated grains.

**Table 1.** Unit cell parameters and offset  $T_c$  (determined at zero resistance) of the YBCO-Ge<sub>x</sub> composite system.

$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	V (Å) <sup>3</sup>	$T_c$ (K) offset	$Anis. = \frac{100(b-a)}{0.5(b+a)}$
0.0	3.82	3.89	11.69	173.71	92	1.81
0.03	3.81	3.88	11.68	172.66	92	1.82
0.06	3.80	3.87	11.67	171.62	89	1.82
0.12	3.78	3.85	11.64	169.40	83	1.83
0.15	3.79	3.86	11.66	170.58	86	1.83
0.20	3.80	3.88	11.68	172.21	92	2.08
1.13	3.82	3.88	11.68	173.12	<77	1.56

Note: Anisotropy  $\left[Anis. = \frac{100(b-a)}{0.5(b+a)}\right]$  is the percentage deviation from tetragonal structure.

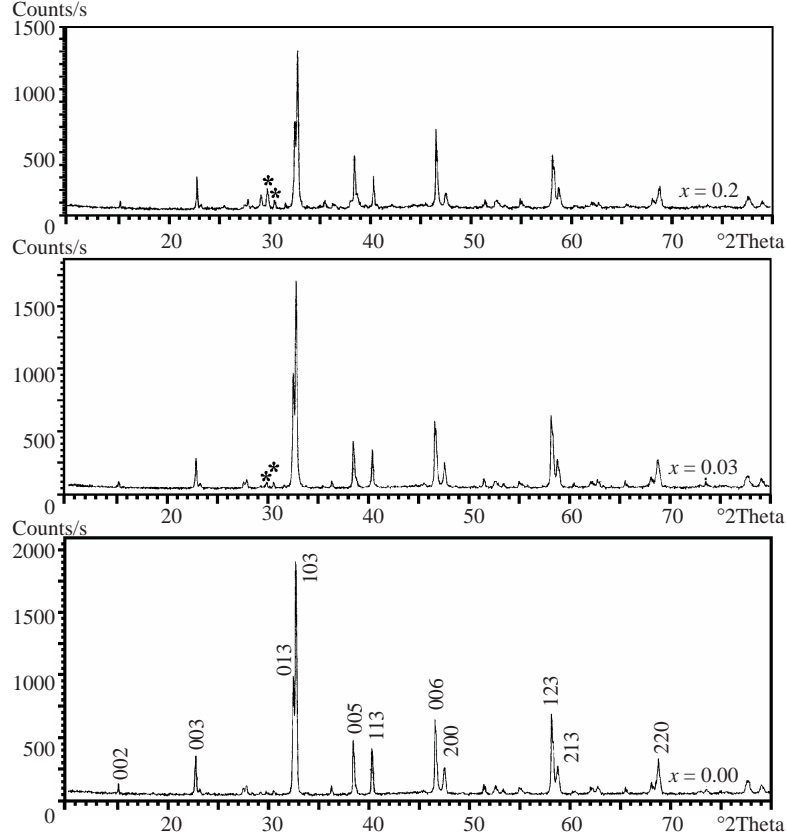
#### 3.2. X-ray diffraction results

X-ray powder diffraction patterns are illustrated in Figures 1, 2. It is clear that the sample with  $x = 0$  has an orthorhombic structure with the phase related to (1-2-3 YBCO) which is responsible for the superconducting state. The characteristic peaks of this phase are indexed as Miller indices ( $hkl$ ). The strongest peaks are (013) and (103) planes as shown in Figure 1.

The samples with Ge content of  $x = 0, 0.03$  and  $0.2$  are polycrystalline and have 1-2-3 orthorhombic phase with  $T_c = 92$  K.

The relative intensities of (00 $l$ ) and ( $hkl$ ) planes are affected due to Ge doping in YBCO with  $x = 0.06, 0.12, 0.15$  and  $1.13$ , where the intensity of (00 $l$ ) family planes are larger for those samples compared with the pure sample ( $x = 0$ ), which is not the case for the other ( $hkl$ ) planes, Figure 2.

This is due to the presence of preferential orientations. The (002), (003), (005), and (006) planes for these samples are grown due to the expected fast growth rate in  $a$  and  $b$  directions and slow growth rate along  $c$ -direction, since the  $c$ -axis is nearly three times as  $a$  and  $b$  axes. This behavior is in good agreement with that reported in ref. [8] where they attributed it to the strongly anisotropic crystal structure of  $Y_1Ba_2Cu_3O_x$  compounds. The resulting intensities are strongly affected, for instance, the peaks corresponding to planes (002), (003), (005) and (006) are amplified while those corresponding to planes (013) and (103) are depressed as indicated in Figure 2. These samples tend to form plate type of single crystals [8] with 1-2-3 orthorhombic phase.



**Figure 1.** X-ray diffraction patterns for  $Y_1Ba_2Cu_3Ge_xO_{7-s}$  where  $x = 0.00$ ,  $x = 0.03$  and  $x = 0.2$ , with orthorhombic phase (\* new phases).

By doping YBCO with Ge, there exist new phases at  $2\theta$  values of  $23.92$ ,  $29.85$  and  $30.60^\circ$  which are indexed to be  $BaCO_3$ ,  $Ba_2GeO_4$  and  $Y_2BaCuO_5$  respectively [9].

The first phase ( $BaCO_3$ ) appears only for the higher Ge content  $x = 1.13$  but the second phase ( $Ba_2GeO_4$ ) and the third phase ( $Y_2BaCuO_5$ ) generally increase with increasing Ge content; Table 2.

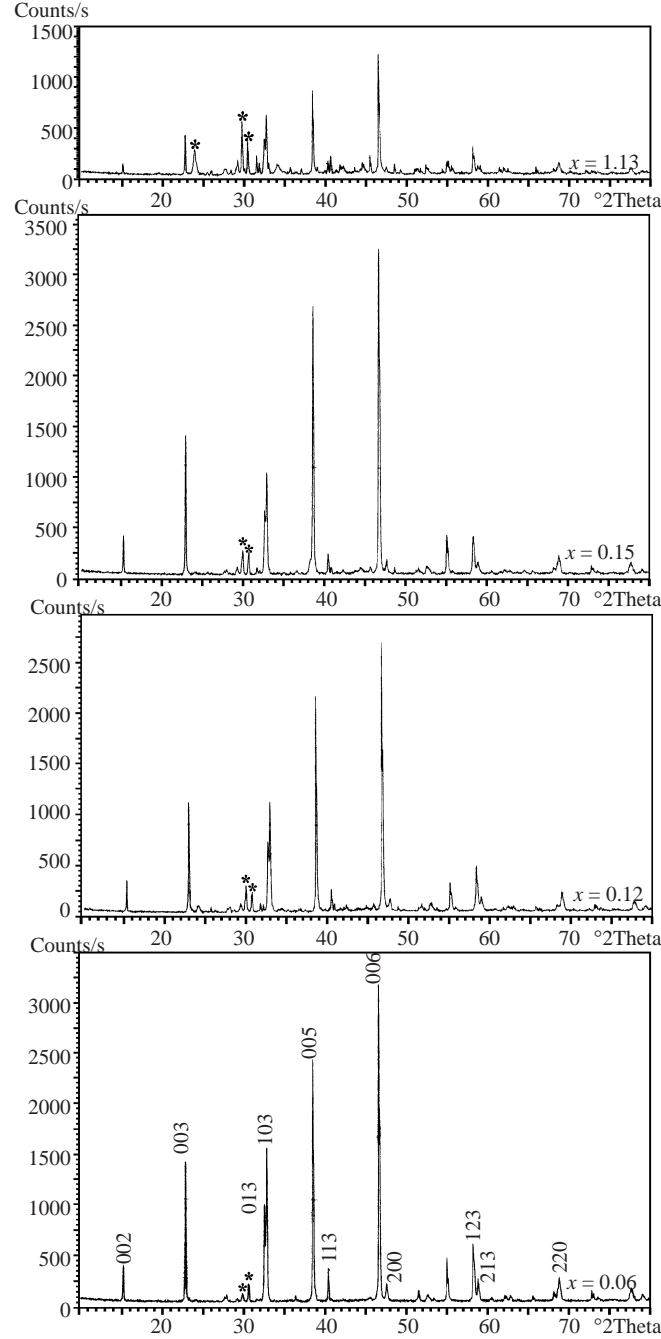
**Table 2.** The relative intensities (relative to plane (103)) of the superconducting phase and Non-superconducting phase of YBCO- $Ge_x$  composite system, obtained from X-ray results.

Sample YBCO	Superconducting phase	Non-Superconducting phase		
		$Ba_2GeO_4$	$Y_2BaCuO_5$	$BaCO_3$
$x = 0.0$	100	0.0	0.0	0.0
$x = 0.03$	100	1.93	2.74	0.0
$x = 0.06$	50	2.20	5.63	0.0
$x = 0.12$	41.31	9.25	6.20	0.0
$x = 0.15$	30.01	7.02	6.70	0.0
$x = 0.20$	100	13.23	5.26	0.0
$x = 1.13$	50.85	43.03	23.41	18.95

These new three phases are created and appear along side with the orthorhombic 1-2-3 structure.

The calculated unit cell parameters of pure YBCO 1-2-3 orthorhombic phase are  $a = 3.82$ ,  $b = 3.89$  and  $c = 11.69 \text{ \AA}$ . The addition of Ge to YBCO produces a depression of the unit cell parameters and so the

volume of the unit cell is depressed, as shown in Table 1. This can be explained as a result of fractional replacement of  $Cu^{2+}$  by  $Ge^{2+}$  (ionic radius of  $Cu^{2+}$  equals  $0.72 \text{ \AA}$  and that of  $Ge^{2+}$  equals  $0.73 \text{ \AA}$ [10]).



**Figure 2.** X-ray diffraction patterns for  $Y_1Ba_2Cu_3Ge_xO_{7-\delta}$  where  $x = 0.06, x = 0.12, x = 0.15$  and  $x = 1.13$ , (\* new phases).

Since  $Ge - O$  bond length is shorter than that of  $Cu - O$  (Atomic number of Ge equals 32 and that of Cu equals 29).

The anisotropy,  $Anis. = \frac{100(b-a)}{0.5(b+a)}$  which is the percentage deviation from tetragonal structure is calculated and listed in Table 1. The anisotropy increases from 1.81 for pure YBCO to 2.08 for Ge content of

$x = 0.2$  but the lowest anisotropy equals 1.56 for the highest Ge content with  $x = 1.13$ .

The changes in the volume of the unit cell and in the anisotropy are related to the  $T_c$  values and the structure of YBCO-Ge composite system, which can be explained as follows:

For low Ge content of  $x = 0.03$  introduced into YBCO, there is a fractional substitution of Cu by Ge atoms, so the result is the reduction of lattice parameters  $a$ ,  $b$ , and  $c$  of 1-2-3 orthorhombic structure. As Ge doping ratio is increased ( $x \geq 0.06$ ), new phases are observed and indexed to be  $BaCO_3$ ,  $Ba_2GeO_4$  and  $Y_2BaCuO_5$ , which are gradually increasing with Ge along side with the 1-2-3 orthorhombic phase.

The superconducting phase, is considered to be related to the height of the strongest peak of the orthorhombic structure of YBCO, which corresponds to (103) plane. The non-superconducting phases, are considered to be related to the heights of the  $BaCO_3$ ,  $Ba_2GeO_4$  and  $Y_2BaCuO_5$  new peaks as listed in Table 2.

From the results in Table 2, it is clear that:

1. For pure YBCO and the samples doped with Ge of  $x = 0.03$  and  $x = 0.2$ , the 1-2-3 superconducting phase is the dominant in the polycrystalline structure.
2. The samples with Ge content of  $x = 0.06$ , 0.12 and 0.15 are multiphase with single crystals of 1-2-3 superconducting phase and an increase of non-superconducting phases. The superconducting phase is mixed with the nonsuperconducting and Ge-phases.
3. In the sample with a higher Ge content  $x = 1.13$  doped in YBCO, there is a decomposition of the structure into two equal separate phases:
  - (i) The first phase is the 1-2-3 orthorhombic which is responsible for superconductivity.
  - (ii) The second phase is due to the creation of  $Ba_2GeO_4$ ,  $Y_2BaCuO_5$  and  $BaCO_3$  which are responsible for the semiconducting and non-superconducting behavior.

### 3.3. Infra red results

The infra-red absorption spectra have been recorded for the YBCO and YBCO-Ge doped samples in the energy range of 200-1000  $cm^{-1}$  as shown in Figure 3.

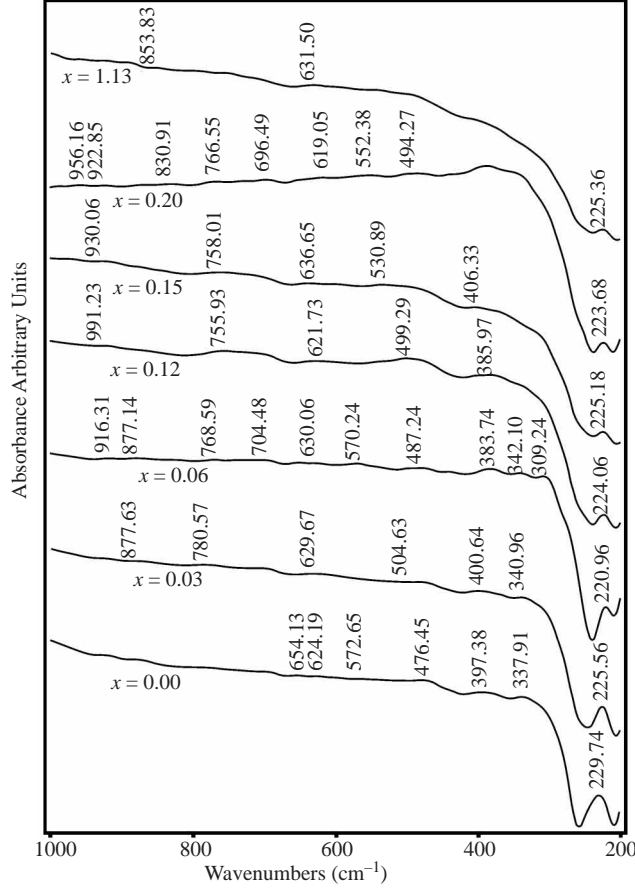
The infra-red active modes are listed in Table 3 for our samples and compared with the reference modes for YBCO in the literature [11-13].

**Table 3.** IR active modes of YBCO and YBCO-Ge<sub>x</sub> composite system.

IR-modes ( $cm^{-1}$ ) [11-13]	Present work IR-modes ( $cm^{-1}$ )						
	YBCO $x = 0.0$	$x = 0.03$	$x = 0.06$	$x = 0.12$	$x = 0.15$	$x = 0.2$	$x = 1.13$
255	229	226	221	224	225	224	225
295	-	-	309	-	-	-	-
335	338	341	342	-	-	-	-
395	397	401	384	386	406	388	-
420	-	-	-	-	-	-	-
470	472	505	487	499	-	494	-
575	-	-	570	-	531	552	-
625	624	630	630	622	637	619	630
690	654	-	704	-	-	696	-
780	-	781	769	756	758	767	-
860	-	878	877	-	-	830	854

From the total number of 21 expected IR-active modes, derived from the factor group analysis of the orthorhombic space group Pmmm [11], only 11 of them namely (255, 295, 335, 395, 420, 470, 575, 625, 690, 780 and 860  $cm^{-1}$ ) are detected in IR-spectrum of YBCO [12]. This can be understood as arising from an

isotropic screening which prevents phonon modes along a and b crystal axes from interacting with IR-electric field, but allows those modes with dipoles oscillating parallel to *c*-axis to appear [13-16].



**Figure 3.** Infra-Red absorption spectra for  $Y_1Ba_2Cu_3Ge_xO_{7-\delta}$  where  $x = 0.00$ ,  $x = 0.03$ ,  $x = 0.06$ ,  $x = 0.12$ ,  $x = 0.15$ ,  $x = 0.20$  and  $x = 1.13$ .

The mode at  $\sim 225 \text{ cm}^{-1}$  is present for all samples and may be due to  $Ba - O$  vibrations.

The mode around  $335 \text{ cm}^{-1}$  appears for YBCO and low Ge doped samples with  $x = 0.03$  and  $x = 0.06$  then disappears for the samples with higher Ge content. This mode is probably due to  $Cu_2 - O_2$  and  $Cu_2 - O_3$  out-of plane bending vibrations [17]. The disappearance of this mode for the samples with higher Ge content is due to the suggested Ge replacement of  $Cu_2$ -sites.

The two peaks around  $400 \text{ cm}^{-1}$  and  $470 \text{ cm}^{-1}$  are possibly concerned with vibrations of  $Cu - O$  basal planes of the pyramids [18]. These two modes disappear for the higher Ge content sample with  $x = 1.13$  which support the hypothesis that Ge occupies fractional sites of  $Cu_2$ . The position and energy of these two modes are also varying with different Ge content, which is another indicator of fractional replacement of  $Cu_2$ -sites by  $Ge^{2+}$  ions.

The modes around  $550 \text{ cm}^{-1}$  and  $570 \text{ cm}^{-1}$  are attributed to the tetragonal phase [18], they approach each other, disappear for pure YBCO and low doped Ge samples, then split into two peaks at  $570 \text{ cm}^{-1}$  and  $\sim 550 \text{ cm}^{-1}$  for samples with Ge content  $x = 0.06$ ,  $x = 0.15$  and  $x = 0.20$ . The behavior of these two modes is complicated and may be concerned with the modes of  $Cu - O$  octahedron bending vibrations.

The peak at  $\sim 630 \text{ cm}^{-1}$  can be assigned probably to the  $O - Cu - O$  stretching related mode for the copper in the mid plane and the adjacent oxygen at the top of the pyramid [18], since the  $Cu - O_4$  bond

length is the shortest in the Cu-O bonds of YBCO unit cell [18]. This peak ( $630\text{ cm}^{-1}$ ) appears also in the Raman-Spectrum [19] and it is attributed to impurity content, particularly of Y2BaCuO5 green phase.

The phonon modes around  $700\text{ cm}^{-1}$ ,  $750\text{ cm}^{-1}$  and  $860\text{ cm}^{-1}$  are mainly due to defects arising from the Ge-phase (Ba2GeO4) and the decomposition of 1-2-3 YBCO superconducting phase into non-superconducting phases as concluded from X-ray diffraction analysis of the prepared YBCO-Ge samples.

According to the superconductor-semiconductor composite model, the YBCO unit cell has a crystal structure with oxide layers of  $\text{CuO}_2$ , BaO and CuO stacked along  $c$ -axis. The  $\text{CuO}_2$  layers are superconducting and the layers CuO and BaO are semiconducting [20]. For simplicity it is considered that YBCO within this model to be constructed of mainly two layers [21]:

- (i) Superconducting layer of  $\text{CuO}_2$ -planes and,
- (ii) Semiconducting layer of CuO-chains and BaO apex oxygen.

The addition of Ge to YBCO will logically increase the semiconducting layers and decrease the superconducting layers. This produces a changeover from metallic to semiconducting behavior of resistance for the higher Ge content  $x = 1.13$  sample. The doping of YBCO with Ge as illustrated from X-ray diffraction patterns, produces mainly two phases, Ba2GeO4 and Y2BaCuO5. This starts to weaken the link between  $\text{CuO}_2$ -planes and CuO-chains through the BaO layer. The result of this is the increase in resistance and decrease in  $T_c$  by doping YBCO with Ge.

The main peculiarity of the YBCO system responsible for the charge transfer effect is the presence of CuO-chains conserving normal charge carriers at all temperatures. The charge transfer occurs between apex oxygen band (BaO), on one hand, and both  $\text{CuO}_2$ -plane and CuO-chain bands on the other hand, so there is an important role of the BaO plane (apex oxygen) for electron-phonon interaction [22-24]. The apex oxygen serves as gates for leaking charge between  $\text{CuO}_2$ -planes and CuO-chains.

The addition of a semiconductor element such as Ge to a superconductor like YBCO, produces a change in the IR-spectrum, as seen in Figure 3, where the superconductivity should be related to electron-phonon coupling. The transition temperature  $T_c$  of a superconductor- semiconductor composite is different from that of the original superconductor. This is an experimental evidence for the importance of the phonon-mediated charge transfer mechanism in high- $T_c$  superconductors along side with the superconductor- semiconductor composite model.

## 4. Conclusion

1. The transition temperature  $T_c$  decreases with Ge doping ( $x < 1.13$ ) and the resistance is transformed from metallic to semiconductor behavior.
2. All the peaks of orthorhombic phase are still present by increasing the Ge contents and new peaks (phases) are produced which are indexed as mainly Ba2GeO4, Y2BaCuO5 (2-1-1) green phase which are semiconducting and non-superconducting phases.
3. Samples with Ge content of  $x = 0.06, 0.12, 0.15$  and  $1.13$  tends to form plate- type of single crystal structure.
4. The I-R absorption modes around  $400\text{ cm}^{-1}$  are attributed to  $\text{CuO}_2$ -planes and that around  $630\text{ cm}^{-1}$  are attributed to CuO-chains. The peaks at  $\sim 700\text{ cm}^{-1}$  to  $860\text{ cm}^{-1}$  may be due to defects as Ba2GeO4 new phase and Y2BaCuO5 green phase.
5. The addition of a semiconductor element such as Ge to a superconductor like YBCO produces a change in IR-spectrum and  $T_c$  of the superconductor - semiconductor YBCO-Ge composite. The superconductivity should be related to electron-phonon interaction.
6. Our results suggest that the presence of certain amount of Ge in the YBCO matrix may produce a superconducting - semiconducting interface without destroying the superconducting properties of the composite system, which could be the base of new electronic devices using thin film technique.



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