

## **ADDITION OF KNO<sub>3</sub> ON YBCO-123 IN ENHANCING THE STRUCTURAL AND MAGNETIC PROPERTIES VIA THERMAL TREATMENT METHOD**

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### **ABSTRACT**

Bulk superconductor of YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  (Y-123) was synthesized by using thermal treatment method. Small amounts (0, 0.1, 0.2 and 0.3 mole) of potassium nitrate (KNO<sub>3</sub>) was added into Y-123 system. The sequel of KNO<sub>3</sub> addition on its critical temperature ( $T_c$ ), phase formation and the microstructure properties were studied. A characterization on the structural properties by means of the x-ray diffraction (XRD) has been investigated. All samples showed an orthorhombic crystal structure with the main phase of Y-123 and Y-211 as a secondary phase. The volume fraction of pure Y-123 is 93.7%. As KNO<sub>3</sub> was added, the percentage of volume fraction decreases. Sample of  $x = 0.2$  give the highest percentage among the added samples with the value of 87.1 %. From electrical properties, the  $T_c$  value has been enhanced as KNO<sub>3</sub> was added. The highest  $T_c$  value (92.7 K) is verified for the sample  $x = 0.2$  with homogeneous grains connectivity. The Y-123 microstructure of the grain growth increases and more homogeneous as KNO<sub>3</sub> was promoted in the system. All in all, these results suggest that the addition of KNO<sub>3</sub> give an enhancement in superconducting properties particularly for the addition of  $x = 0.2$  mole.

*Keywords: Potassium Nitrate; superconductor; thermal treatment; YBCO*

### **INTRODUCTION**

Superconductor continues to be a great frontier of scientific discovery. The superconductivity phenomenon was first discovered in 1911. In 1987, YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> (Y-

123) ceramics was found to be the first ceramic with the critical temperature ( $T_c = 92$  K) above liquid nitrogen by Wu et al. [1] and until now intense researches are still continuously being reported for this material worldwide interest. The properties of zero electrical resistance as well as magnetic flux exclusion in superconductor make it one of the most promising materials in science technology. One of the best applications to be mentioned is the role of a superconductor in advanced medical technologies. Magnetic Resistance Imaging (MRI) for an instance is one of the most powerful application in diagnostic medical imaging. The superconducting magnet in MRI is able to reach the field values that cannot be reached by another typical conventional magnet. As a consequence a high quality, high resolutions and precise imaging is produced as an outcome [2] and had been proven to be helpful by the physician such as in diagnosing tumors, sclerosis and oedemas.

Different synthesis techniques have been used in preparing the superconductor. Dry method such as solid state method [3], [4] and wet method i.e. co-precipitate [5] and thermal treatment [6] are among several methods that can be deployed. Recently, synthesization of a superconductor via thermal treatment method gained much attention. In this simple method, an aqueous solution together with polymer was used as capping agent [6] and to reduce agglomeration of the particles [7]. Thermal treatment is a simple method, low cost and can be used to obtain fine powder [6]. The introduction of an oxidizing atmosphere during thermal treatment may give higher  $T_c$  up to a maximum value of 92 K [8]. The  $T_c$  is also sensitive to the doping and impurities where the added element might suppress the superconductivity [9].

The objective of this research was to study the effect of potassium nitrate ( $KNO_3$ ) addition on Y-123 samples. The results of the superconducting properties, phase formation and microstructure properties of  $YBa_2Cu_3O_{7-\delta}$  with the addition of  $KNO_3$  ( $x = 0, 0.1, 0.2$  and  $0.3$  mole) is reported in this paper.

## **EXPERIMENTAL DETAILS**

In this experiment, the  $YBa_2Cu_3O_7$  bulk sample was synthesized by using thermal treatment method. The sample was fabricated with metal nitrates materials as starting materials, polyvinyl pyrrolidon (PVP) as capping agent and deionized water as solvent. The starting materials used for the sample were Yttrium (III) nitrate hexadrate ( $Y(NO_3)_3 \cdot 6H_2O$ ), Barium nitrate ( $Ba(NO_3)_2$ ), Copper (II) nitrate hemi-pentahydrate ( $Cu(NO_3)_2 \cdot 5H_2O$ ) and polyvinyl pyrrolidon (PVP). All of the materials were purchased from Alfa Aesar. In this method, an aqueous solution of the starting materials together with the polyvinyl pyrrolidon (PVP) and 300 ml deionized water were mixed and dissolved evenly. The solutions were stirred continuously for 2 h at the temperature of 80 °C to get the homogenous mixture. A green-blue solution was obtained from the first step. After 2 h being stirred, the sample was then dried in an oven at 110 °C for 24 h. The solid-like green gel obtained was then crushed and ground to get the fine powder and pre-calcined in a box furnace for 4 h at 600 °C. The sample was then ground and calcined again at 910 °C for 24 h and cooled in air at the rate of 1 °C per min. During the calcination process, the PVP and all of the organic compound was removed and the

metallic oxide was formed [6]. The powder was then ground and palletized before being sintered in flowing O<sub>2</sub> at 980 °C for 24 h. The potassium material was added during the palletization process. The characterization of the sample can be divided into two which are physical and electrical properties. For the physical properties the crystal structure was determined by using X-ray Diffraction (XRD) obtained using Xpert Pro Panalytical Philips DY 1861. The structure and the morphology characterization were made by using Scanning Electron Microscopy (SEM) together with the Energy Dispersive X-ray (EDX) image. In term of the electrical properties, the critical temperature was measured by using AC Susceptibility (ACS).

## RESULTS AND DISCUSSION

The XRD pattern of Y-123 with KNO<sub>3</sub> addition is shown in Figure 1. All peaks in each diffraction pattern are indexed to Y-123 phase with the highest intensity diffraction pattern at  $2\theta = 32.90^\circ - 33.12^\circ$ . The addition of KNO<sub>3</sub> into Y-123 system does not change the polycrystalline pattern of the diffractograms unless some extra peaks are assigned in the pattern which indicate the appearance of Y-211, Y-247 phase and some impurities which belong to BaCuO. The presence of Y-211 and Y-247 secondary phase started to present in  $x = 0.1$  and become decreases as the addition of KNO<sub>3</sub> increases. The KNO<sub>3</sub> were not observed in the spectrum as the wt. % of each addition is too small [10]. The presence of Y-211 phase was also stated by Dihom et al. [6] in 2017. This phase is expected to form during the solidification of pores in cooling process of Y-123 phase [11]. The volume fraction of Y-123 decreases as KNO<sub>3</sub> was added, however for sample  $x = 0.2$  gives the highest value among the added samples. The volume fraction and phases present on samples are tabulated in Table 1.

Table 1: Volume fraction of the phases present on samples with potassium concentration (mole),  $x = 0.0, 0.1, 0.2$  and  $0.3$

Potassium concentration (mole)	Volume fraction (%)			
	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub>	Y <sub>2</sub> Ba <sub>1</sub> Cu <sub>1</sub> O <sub>5</sub>	YBa <sub>2</sub> Cu <sub>4</sub> O <sub>8</sub>	BaCuO <sub>2</sub>
0	93.7	-	-	6.3
0.1	58.8	15.6	10.3	15.3
0.2	87.1	12.9	-	-
0.3	80.5	-	-	19.5

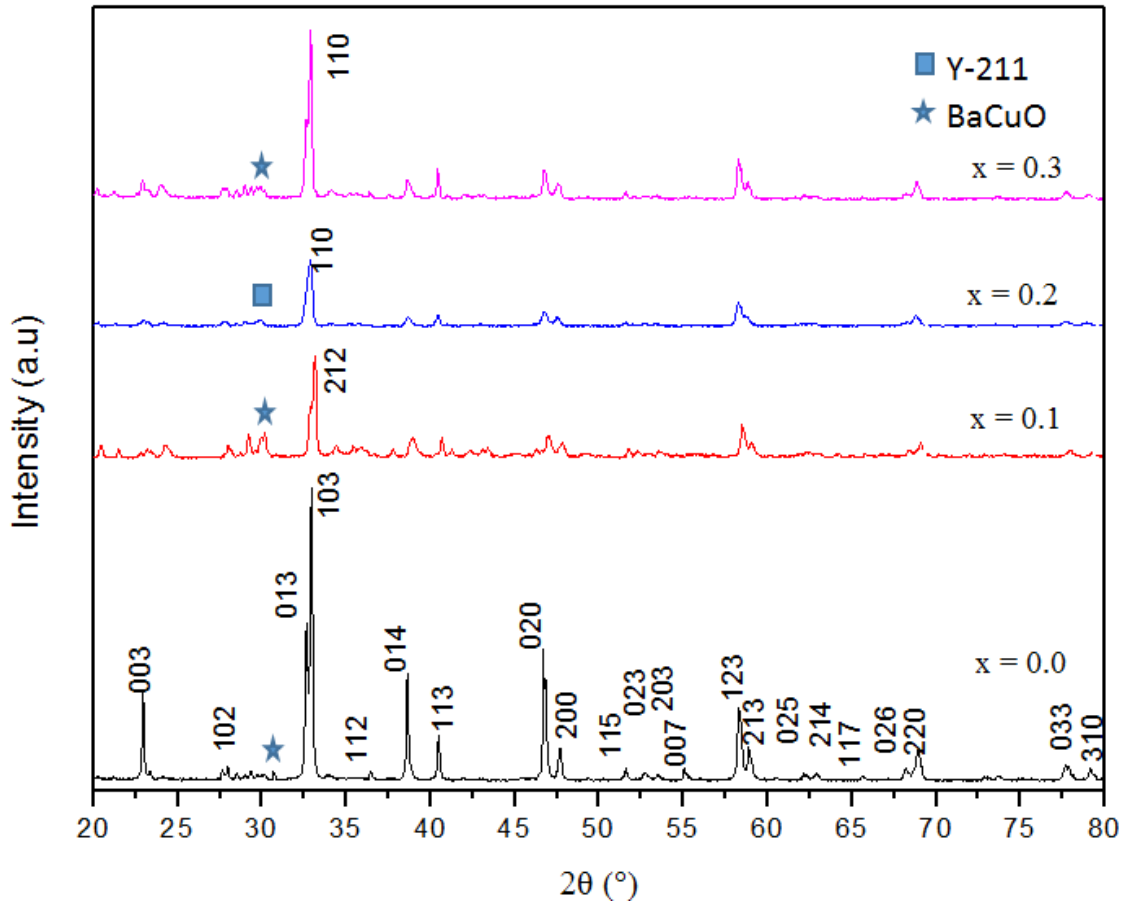


Figure 1: The XRD pattern for Y-123 samples added with (a) 0.0 mol (b) 0.1 mol (c) 0.2 mol (d) 0.3 mol of KNO<sub>3</sub>

The lattice parameter and the unit cell volume of all samples were determined by Rietveld refinement analysis using X'pert high score software and tabulated in Table 2. Lattice parameter for  $a$  and  $b$  does not show systematic change for each sample. Meanwhile, for lattice parameter  $c$ , there showed a slight change on every addition. The orthorhombicity was calculated by using formula  $[(b - a)/(a + b)]$  where  $a$  and  $b$  is the lattice constant  $a$  and lattice constant  $b$ , respectively [6]. The orthorhombicity can be diminished with the changes occur on lattice constant, due to the oxygen content in the sample [12]. Values of the lattice parameter proves that all the samples have orthorhombic structure. These values plays important role in determining the superconductivity below 77 K [13] The average crystallite size can be calculated using Scherrer equation,  $D_{hkl} = k\lambda / \beta \cos\theta$ , where  $k$  is shape factor (0.9),  $\lambda$  is the wavelength of XRD CuK $\alpha$  radiation source,  $\beta$  is the highest intensity of the main peak and  $\theta$  is the bragg angle. The crystallite size was unsystematically changed upon the addition of KNO<sub>3</sub>.

Table 2: Lattice parameters of the samples with potassium concentration (mole),  $x = 0.0, 0.1, 0.2$  and  $0.3$

Potassium concentration (mole)	Lattice parameter			Unit cell volume ( $\text{\AA}^3$ )	Orthorhombicity $[(b - a)/(a + b)]$	Crystallite size (nm)
	$a(\text{\AA})$	$b(\text{\AA})$	$c(\text{\AA})$			
0.0	3.8206	3.8890	11.6775	173.5130	0.0088	920.0
0.1	3.8305	3.8950	11.6715	174.1422	0.0083	663.0
0.2	3.8361	3.8913	11.6836	174.4109	0.0071	443.0
0.3	3.8275	3.8880	11.6643	173.5806	0.0078	804.0

The ac conductivity was measured by using ac susceptometer (ACS). Figure 2 shows the normalized susceptibility against temperature for Y-123 with  $x = 0, 0.1, 0.2, 0.3$  mole of  $\text{KNO}_3$ . The real part or in-phase,  $\chi'$  represents the penetration of ac magnetic field into the superconductor while imaginary part or out-of-phase while  $\chi''$  represents the dissipation of AC in sample.  $T_{c\text{-onset}}$  involved within the grain (intra-grain) and  $T_{cj}$  involved across the grain (inter-grain) where exclusion of flux from the inner part of superconductor occurs. Meanwhile, the peak formed in  $\chi''$  represents the coupling peak temperature,  $T_p$  [14]. The variation of  $T_{c\text{-onset}}$  and  $T_{cj}$  are as referred in Table 3.

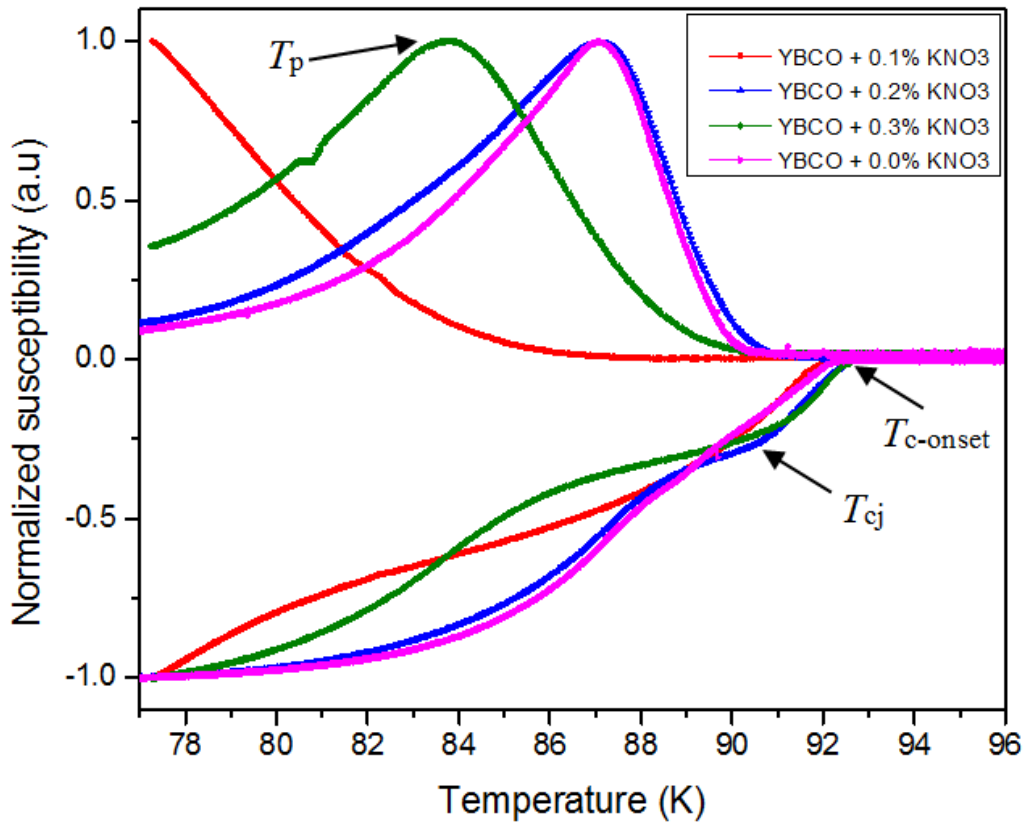


Figure 2: Graph of normalization of susceptibility of  $\chi'$  and  $\chi''$  against temperature

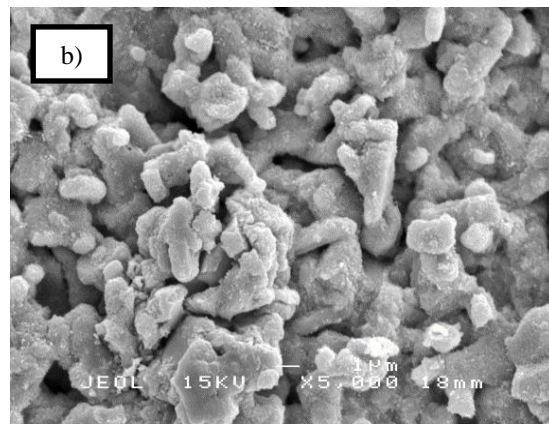
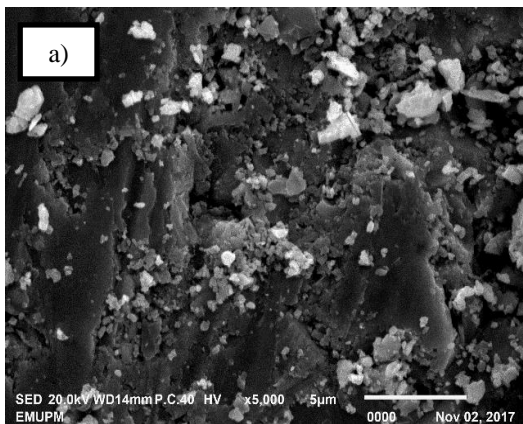
Table 3:  $T_{c\text{-onset}}$ ,  $T_{cj}$  and  $T_p$  for Y-123 +  $x$  mol of  $\text{KNO}_3$

Potassium concentration (mole)	$T_{c\text{-onset}}$	$T_p$	$T_{cj}$
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0.0	92.4	87.1	-
0.1	92.1	-	77.0
0.2	92.7	87.2	87.5
0.3	92.6	83.7	84.2

Based on Figure 2, sample  $x = 0.0$  exhibit a single step transition which showed a strong coupling between the grain [15]. Moreover, double steps transition can be seen in all added samples. The double steps transitions indicate the presence of Y-211 phase [12] and happened due to the shielding of flux by intra-grain currents as the temperature decreases [16]. The sample with  $x = 0.0$  and  $x = 0.2$  has stronger grain coupling by referring to its  $T_p$  which broadens more to the right side of the graph. From Table 3, it can be seen that the addition of the potassium can enhance the  $T_c$  of the sample. The changes of the  $T_c$  is related to the stoichiometric and defect problems during growth of the sample [17] which can be related to the decreasing of  $\text{CuO}_2$  plane and decrease in the  $\text{CuO}$  chain [11]. The addition of potassium enhances the grain homogeneity and thus increase the  $T_{cj}$  value.

Figure 3 shows SEM images for the formation of grain growth in  $x = 0, 0.1, 0.2, 0.3$  mole of  $\text{KNO}_3$  added to Y-123 at 5000x magnification. The overall shape of the grain shows an irregular and randomly oriented. Pure sample has a small grain size with high porosity. Further increase of  $\text{KNO}_3$  addition gives a larger average grain size, less porosity, much homogeneity and well-connected grains. The highest addition ( $x = 0.3$ ) showed the highest average grain size for about  $2.32 \mu\text{m}$  as compared to the pure sample which only  $1.27 \mu\text{m}$ . The value of the average grain size was calculated by using Image J software and can be referred to the Table 4. The addition of  $\text{KNO}_3$  promotes the grain growth, phase formation [18] and enhance the homogeneity of samples [11]. Based on EDX analysis, there is no evidence about the presence of  $\text{KNO}_3$  in Y-123 matrix in SEM. This expected to happen as it might located in between the grain boundaries [11].



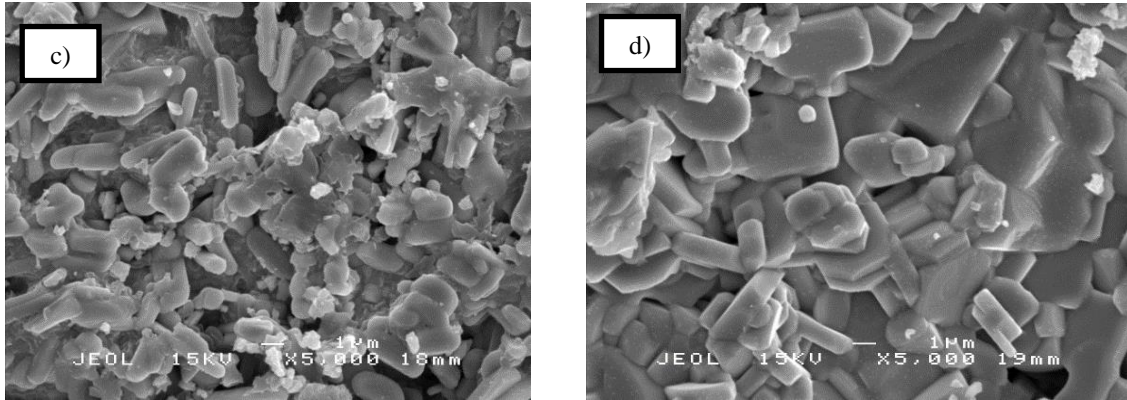


Figure 3: SEM images at surface morphology area of Y-123 samples added with (a) 0.0 mol (b) 0.1 mol (c) 0.2 mol (d) 0.3 mol of  $\text{KNO}_3$  at 5000x magnification

Table 4: Average grain size for  $x = 0, 0.1, 0.2, 0.3$  mole of  $\text{KNO}_3$

Potassium concentration (mole)	Average grain size, $\mu\text{m}$
0.0	1.2689
0.1	1.8446
0.2	1.9859
0.3	2.3254

### CONCLUSIONS

An orthorhombic structure of YBCO has been successfully synthesized by using thermal treatment method. All peaks were successfully indexed to Y-123 peaks as the main peak except for sample  $x = 0.2 \text{ KNO}_3$  with a secondary phase of Y-211 and BaCuO. The grain size of all samples increases with the addition of potassium which proves that the addition helps in promoting the homogeneity and the connectivity between the grains. While the resistivity results also showed an enhancement of the  $T_c$  value with the optimum concentration of  $x = 0.2$  mole.

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