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Effects of citrate to nitrate ratio on superconducting properties of $YBa_2Cu_3O_{7-\delta}$ prepared via auto-combustion reaction

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ABSTRACT – A series of $YBa_2Cu_3O_{7-\delta}$ was prepared via citrate-nitrate auto-combustion reaction. Metals nitrates were mixed with calculated amount of citric acid to obtain gels with citrate to nitrate ratio, c/n ranged from 0.3 to 0.9. The gel was transformed to fine ashes through auto-combustion reaction to yield $YBa_2Cu_3O_{7-\delta}$ during calcination. The XRD analysis revealed that each sample yielded orthorhombic polycrystalline of $YBa_2Cu_3O_{7-\delta}$ which was confirmed by EDX analysis. Each samples achieved zero resistivity in different manners. Samples with c/n = 0.3 and 0.5 behave more like normal metallic while samples with c/n = 0.6, 0.7 and 0.9 behaved like semiconductor.

1. INTRODUCTION

Yttrium barium copper oxide ($YBa_2Cu_3O_{7-\delta}$) is classified as high temperature superconducting material due to its ability to achieve zero electrical resistivity at temperatures above 77 K. Discovered in 1987, the critical temperature, T_C of $YBa_2Cu_3O_{7-\delta}$ synthesized using solid state reaction was found to be ~93 K [1]. This reaction however consumes a lot of time and energy since the precursor powders need to be ground repeatedly to achieve homogeneous mixture and requires higher calcination temperature to yield $YBa_2Cu_3O_{7-\delta}$ phase. Hence there have been many attempts to develop new synthesis method to obtain highly pure $YBa_2Cu_3O_{7-\delta}$ [2]. One interesting method that can be employed is citrate-nitrate auto-combustion reaction which is a powerful technique to obtain high purity samples since the reaction generates enough heat to volatize all low boiling point impurities [3]. The reaction is also having low processing costs, simple exothermic reaction, and can be used to yield new materials. The mechanism of the auto-combustion reaction is quite complex and highly influenced by citrate to nitrate ratio, c/n. Li et al. [4] in their study on synthesis of Al_2O_3 reported that excess or limited amount of citric acid results in different characteristics of combustion reaction which may produce impurities. Meanwhile Chandradass and Kim [5] had proposed that the optimum combustion reaction could occur when the oxidizer (metal nitrates) and fuel (citric acid) is stoichiometrically balanced. Thus, the effects of c/n towards the structural and superconducting properties of $YBa_2Cu_3O_{7-\delta}$ needed to be studied. In this work, the citrate-nitrate auto-combustion reaction was used to synthesize $YBa_2Cu_3O_{7-\delta}$ nanoparticles and the effects of c/n ratio were discussed.

2. METHODOLOGY

Analytical grade of $Y(NO_3)_3{\cdot}6H_2O$, $Ba(NO_3)_2$, and $Cu(NO_3)_2{\cdot}3H_2O$ reagent powders were dissolved in distilled water to prepare 0.5, 0.25 and 0.5 M of Y, Ba and Cu nitrate aqueous solutions respectively. These solutions then were mixed together by the mole ratio of Y:Ba:Cu = 1:2:3. An appropriate amount of citric acid was added into the mixture to alter the citrate-nitrate ratio, c/n value from 0.3 to 0.9 and its pH was adjusted to pH≈7 by adding liquor ammonia. Resultant solution then was dried at 250 °C on the hot plate with infrared lamp on top to provide uniform heating. After the auto-combustion reaction occurred, the as-prepared ashes powder was calcined at 900 °C under ambient atmosphere for 1 hour and let in the furnace cooling. The X-ray diffraction (XRD) for the calcined powder phase identification and crystallite size estimation was carried out using Ni-filtered Co Kα radiation by Bruker D8-advanced XRD machine. The peak position and intensities were obtained between 20° and 70° with a velocity of 0.02° s^{-1}. Energy dispersive X-ray (EDX) from Zeiss Ultra 40XB, was used to determine elemental distribution in the powder. The critical temperature, T_C, of the samples was measured using 4 point probe at liquid nitrogen temperature.

3. RESULTS AND DISCUSSIONS

Figure 1 shows the XRD patterns of $YBa_2Cu_3O_{7-\delta}$ samples with different c/n ratio. Vertical bars at bottom of the figure represent Bragg's diffraction angle of standard $YBa_2Cu_3O_{7-\delta}$ with lattice constants of a = 0.3877, b = 0.3827 and c = 11.6880 Å with Pmmm 47 symmetry. Each XRD pattern indicates the existence of polycrystalline $YBa_2Cu_3O_{7-\delta}$ phase. It can be observed that the XRD peaks for c/n = 0.6 and 0.7 samples occur at exact positions for standard $YBa_2Cu_3O_{7-\delta}$ phase prepared by Pathack et al. [1]. Few impurity peaks indicated by black dots in Figure 1 can be detected on XRD patterns of the samples with c/n = 0.3, 0.5 and 0.9 where these peaks can be assigned to YBaO and BaCuO phases. The atomic number of each element in each sample is listed in Table 1. From the atomic ratio of all samples, it was confirmed that samples with c/n = 0.6 and 0.7 had yielded pure $YBa_2Cu_3O_{7-\delta}$ compound. This is in good agreement with the XRD data. While the existence of excess Y, Ba and Cu in samples with c/n = 0.3 and 0.5 is the evidence of the presence of YBaO and BaCuO impurities. The BaCuO impurity was also apparent in sample with c/n = 0.9 as the ratio of Ba exceeded the expected value.

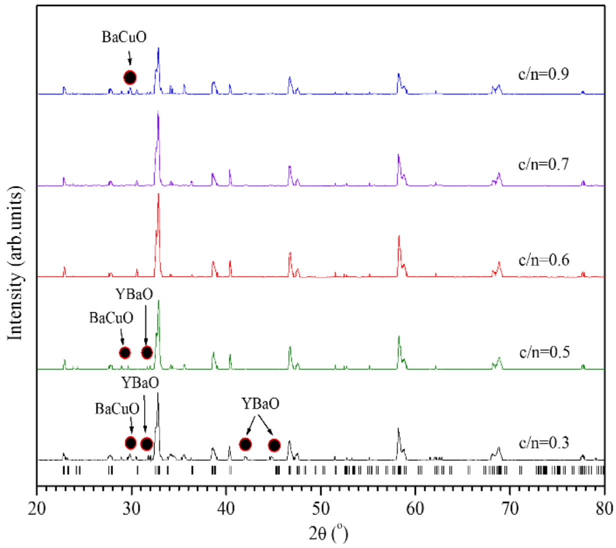

Figure 1 XRD patterns of $YBa_2Cu_3O_{7-\delta}$ samples after being calcination process

Table 1 EDX analysis of the $YBa_2Cu_3O_{7-\delta}$ samples

Sample (c/n)	Atomic (at. %)				Atomic Ratio
	Y	Ba	Cu	O	Y:Ba:Cu
0.3	11.27	14.13	17.66	56.93	1:1.25:1.57
0.5	11.75	13.51	18.07	58.67	1:1.15:1.54
0.6	8.37	16.83	24.38	51.02	1:2.01:2.91
0.7	8.20	16.45	24.67	50.67	1.0:2.0:3.0
0.9	6.89	16.95	19.12	57.04	1:2.46:2.78

Figure 2 shows the temperature dependence of electrical resistivity for $YBa_2Cu_3O_{7-\delta}$ samples with different c/n values. As can be seen from this figure, the resistivity of each sample was reduced to zero in different manners. The resistivity is decreased and stabilized before abruptly reduced to zero in c/n = 0.3 and 0.5 samples. At temperature above the T_C, the relation between resistivity and temperature of these samples is more likely normal metallic behavior. On the other hand, samples with c/n = 0.6, 0.7 and 0.9 were behaved like semiconductor as the resistivity is consistently decreased and then rapidly dropped to zero at the T_C. Inset in Figure 2 show the T_C onset and T_C zero values of the samples which are labelled by black and blue arrows respectively. The T_C onset is increased from 77.5 to 91.8 K as c/n is increased from 0.3 to 0.7. On the other hand, T_C onset decreased to 83.6 K in sample with c/n = 0.9. The T_C zero of the samples also vary by the same pattern. The transition widths are 2.5, 0.7, 1.0, 1.1 and 1.6 K for samples with c/n = 0.3, 0.5, 0.6, 0.7 and 0.9 respectively. The highest T_C zero is achieved in sample having c/n = 0.7 followed by the sample having c/n = 0.6. This is due to high purity of $YBa_2Cu_3O_{7-\delta}$ with oxygen deficiencies at around 0.2. Existence of non-superconducting YBaO and BaCuO impurities in samples having c/n = 0.3, 0.5 and 0.9 obstructed superconducting current to flow at T_C zero for typical $YBa_2Cu_3O_{7-\delta}$ superconductor.

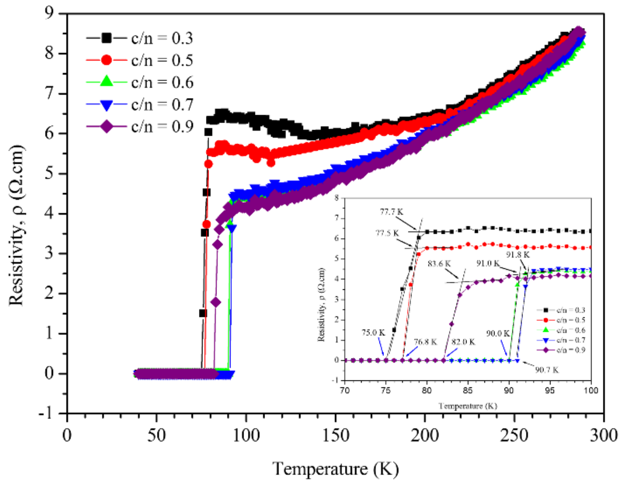

Figure 2 Temperature dependence resistivity of $YBa_2Cu_3O_{7-\delta}$ samples with different c/n. Inset shows T_C onset and T_C zero of the $YBa_2Cu_3O_{7-\delta}$ samples

4. CONCLUSIONS

The $YBa_2Cu_3O_{7-\delta}$ sample prepared using c/n = 0.7 was shown to have the highest purity compare to other samples. The sample exhibited T_C zero of 91.8 K with sharp transition width.

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