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The Effect of the Grinding Method on the Physical Properties of Y134 Superconductor Doped Manganese Oxide Prepared by Solid State Reaction

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Abstract

The synthesis of Y134 cuprate superconductor ($YBa_3Cu_4O_{9.5}$) doped with manganese oxide powder (Mn_3O_4) was done by two solid state reaction processes used grinding by ball milling and mortar. Then, we characterized the physical properties by SEM, EDX, XRD, iodometric titration and the resistivity measurement. The SEM and EDX showed that the samples prepared by ball milling were more homogeneous and compact than preparing by mortar. The results of XRD referred to orthorhombic structures for all samples. It showed that the manganese oxide unaffected the crystal structure of Y_{134} superconductor. The resistivity measurements showed that the ball milling samples had the upward trend of onset critical temperature from 93.0-98.7 K for adding bigger amount of manganese oxide, being higher than one done by mortar at 91.0-92.7 K. It was in same trend as average grain size and Cu^{3+}/Cu^{2+} ratio. Moreover, ball milling could increase efficiency of manganese oxide doping confirmed by the best critical temperature of ball milling sample doped with 0.015 mol of manganese oxide as 98.7 K.

Keywords: Superconductor, Cuprate, Critical temperature, Ball milling.

1. Introduction

Superconductivity was discovered by Heike Kamerlingh-Onnes in 1911 (1). It's the phenomenon that a material loses electrical resistance on cooling below the critical temperature (T_c). Later, the high-temperature superconductivity in cuprate oxides ceramic was discovered by Bednorz and Muller in 1986. It was $La_{2-x}Ba_xCuO_4$ with a higher transition temperature at 57 K. It was formed of perovskite unit cells and had CuO_2 plane was termed the conduction plane.

A year after the first high-T_c superconductor discovery, Chu and co-workers replaced atoms of lanthanum in the compound by yttrium in nominal composition $Y_{1.2}Ba_{0.8}CuO_{4-y}$. They found the popular composition $YBa_2Cu_3O_{7-y}$ that had superconductivity at 90 K. It was high enough to use liquid nitrogen for cooling which was lower cost than liquid helium using extremely. In 2014, $YBa_3Cu_4O_x$ superconductor or Y134 in stoichiometric ratio of Y, Ba, and Cu at 1:3:4 was synthesized by solid state reaction for comparison with Y123 superconductor in a stoichiometric ratio 1:2:3 which was the main of YBaCuO family compound. The results showed that the Y134 superconductor had higher phase transition temperature at 92.5 K (2, 3). Therefore, we were interested in Y134 compound in this research.

Another important technique to improve the physical properties of superconductor was an ionic substitution by metal oxide. It considerably affected to the concentration of oxygen in the conduction planes which related to the critical temperature of superconductor.

In 2015, Mn_3O_4 doping on Y123 compound showed significant increase of critical temperature to 119 K when it was doped with slight concentrations of nano manganese oxide (Mn_3O_4) (4, 5). It was probable that both Mn_3O_4 and particle size had really affected an increase of critical temperature.

For the particle size reduction, a Ball Milling was an efficient grinding which widely used for ceramics preparing. It was reported that the ball milling machine produced nanoparticles by impact as the balls drop from near the top of the shell (6). In 2017, it was used to prepare the Y134 superconductor (7). It reduced the particle size and holes between grains of superconductor and efficiently mixed all elements for a homogeneous compound. The use of machinery – ball milling was proven to be effective than the traditional method by alumina mortar and manual labor.

This paper studied the effect of Mn_3O_4 doping on Y134 compound by using ball milling method and compared to the mortar using. All synthesized samples were characterized by SEM, EDX, XRD, the iodometric titration and the electrical resistivity measurement.

2. Materials and Experiment

The two groups of $YBa_3Cu_4O_{9.5}$ + xMn_3O_4 series with x=0, 0.005, 0.010 and 0.015 moles of manganese oxide, consisting of mortar group (MT) and ball milling group (BM) were prepared from high-purity powder of Y_2O_3, $BaCO_3$, CuO, and Mn_3O_4 by solid state reaction. The mixture of Y_2O_3, $BaCO_3$ and CuO powders were twice heated by calcination processing at 950°C for 24 hours. The calcinated compounds of each group were doped with Mn_3O_4 in specific concentrations by mortar and wet ball milling with alumina balls, using speed at 1,200 rpm for 24 hours. then dry the doped samples by magnetic stirrer hot plate mixer before pressing into pellets with 20 mm in diameter and 5 mm in thickness by 15,000 N/m^2 of compression. All the pellets were heated by the sintering at 950°C for 24 hours. and annealing at 500°C for 24 hours. in normal atmosphere. The samples of $YBa_3Cu_4O_{9.5}$+ xMn_3O_4 were investigated for the physical properties characterization by SEM micrograph, EDX analysis (JEOL JSM-IT300), XRD (D8-Discover), iodometric titration and four points probe technique according to Van Der Pauw method of resistivity measurement in liquid nitrogen cooling system by using electric current as 200 mA.

3. Results and Discussion

All obtainable samples were examined on physical properties by SEM, EDX, XRD structure characterization, titration for Cu^{3+}/Cu^{2+} ratio definition, and the resistivity measurement.

3.1 The SEM photographs

The SEM photographs in Figure 1 and Figure 2 showed morphology of the samples. The average grain sizes of samples by using ImageJ 1.52a were 3.609±1.993, 3.829±2.318, 4.311± 1.965, 4.371±1.773 µm for 0, 0.005, 0.010, 0.015 mol of doping in samples prepared by mortar (MT) and 3.107±0.795, 4.110±1.646, 4.588±1.442, 5.112±1.392 µm for samples in ball milling group (BM). The grain size of them was the upward trend in more Mn_3O_4 in both cases shown in Figure 3. They showed that the Mn_3O_4 affected on effectiveness of crystallization.

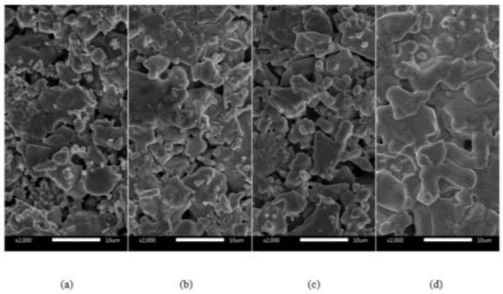

Figure 1 SEM photographs of the mortar group. (a) Y134, (b) Y134+0.005Mn_3O_4, (c) Y134+0.010Mn_3O_4, (d) Y134+0.015Mn_3O_4.

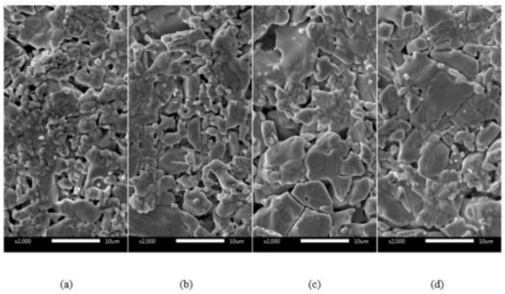

Figure 2 SEM photographs of the ball milling group. (a) Y134, (b) Y134+0.005Mn_3O_4, (c) Y134+0.010Mn_3O_4, (d) Y134+0.015Mn_3O_4.

The standard deviations of grain size represented the distribution of grain sizes in the mortar group was more different than that of the ball milling group. Moreover, porosity on ball milling group surfaces was smaller. They showed the efficiency of ball milling method was greater than one using mortar.

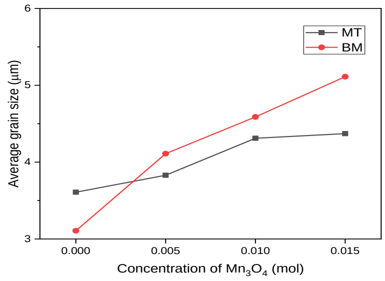

Figure 3 The concentration of Mn_3O_4 versus the average grain size.

Table 1 Stoichiometric ratio of samples.

Samples	Stoichiometric ratio (%error)				
	Y	Ba	Cu	O	Mn
Y134 (MT)	1.00 (0.00%)	2.46 (18.00%)	2.92 (27.00%)	8.29 (12.74%)	0.00 (0.00%)
Y134 + $0.005Mn_3O_4$ (MT)	1.00 (0.00%)	3.08 (2.67%)	3.95 (1.25%)	10.06 (5.67%)	0.03 (50.00%)
Y134 + $0.010Mn_3O_4$ (MT)	1.00 (0.00%)	2.88 (4.00%)	3.73 (6.75%)	9.12 (4.40%)	0.05 (66.67%)
Y134 + $0.015Mn_3O_4$ (MT)	1.00 (0.00%)	2.66 (11.33%)	3.45 (13.75%)	8.55 (10.56%)	0.04 (20.00%)
Y134 (BM)	1.00 (0.00%)	2.95 (1.67%)	3.94 (1.50%)	9.64 (1.47%)	0.00 (0.00%)
Y134 + $0.005Mn_3O_4$ (BM)	1.00 (0.00%)	2.84 (5.33%)	3.84 (4.00%)	9.29 (2.42%)	0.02 (0.00%)
Y134 + $0.010Mn_3O_4$ (BM)	1.00 (0.00%)	2.98 (0.67%)	3.86 (3.50%)	9.32 (3.35%)	0.02 (33.33%)
Y134 + $0.015Mn_3O_4$ (BM)	1.00 (0.00%)	3.15 (5.00%)	4.03 (0.75%)	9.89 (3.45%)	0.06 (20.00%)

Table 2 Moles of copper of samples.

Samples	Moles of copper			Oxygen content (O_y)
	Cu^{2+} ($\times10^3$)	Cu^{3+} ($\times10^3$)	Cu^{3+}/Cu^{2+}	
Y134 (MT)	7.198	1.407	0.195	8.827
Y134 + $0.005Mn_3O_4$ (MT)	7.098	1.621	0.228	8.872
Y134 + $0.010Mn_3O_4$ (MT)	6.937	1.962	0.283	8.941
Y134 + $0.015Mn_3O_4$ (MT)	6.993	1.885	0.270	8.925
Y134 (BM)	6.814	1.886	0.277	8.934
Y134 + $0.005Mn_3O_4$ (BM)	6.283	2.385	0.380	9.050
Y134 + $0.010Mn_3O_4$ (BM)	6.681	2.051	0.307	8.970
Y134 + $0.015Mn_3O_4$ (BM)	7.028	1.886	0.268	8.923

3.2 The EDX analysis

The EDX results supported the information from SEM. The average stoichiometric ratio of samples was shown in Table 1. The element ratio comparison between samples and chemical formulas showed that experimental ratios in samples ground by ball milling were similar to their form than samples from the mortar method that showed mixing capability of ball milling which was used for cuprate superconductor preparing. The error might cause by an unsteady process and using too small amounts of substrate. Moreover, the purity of samples without other substances from ball provided the hardness of alumina balls.

3.3 The XRD structure characterization

The graph of XRD at room temperature in 2-theta angle vary from 10° - 90° in Figure 4 showed the same pattern of peaks for all samples compared to Y134 superconductor in Chainok's researches (2, 3). They demonstrated the same type of crystal structure. The orthorhombic structures of all samples were defined by peaks analysis consisting of a=3.80 Å, b=3.88 Å, and c=15.25 Å, approximately.

3.4 The iodometric titration

We titrated for determination of iodine's moles by using 0.0308 M of sodium thiosulphate, then characterized Cu^{3+}/Cu^{2+} ratio in structure of the samples. The Cu^{3+}/Cu^{2+} ratio related to CuO_2 planes in cuprate superconductor and oxygen content in structure.

The results were shown in Table 2 demonstrated the slight increase of Cu^{3+}/Cu^{2+} ratio in Figure 5 when we doped Mn_3O_4 in Y134 superconductor and the oxygen contents were calculated from them. These results showed that the Y134 doped with Mn_3O_4 had more CuO_2 planes conformity in structure than non-doping. It was the result of the substitution by Mn atom in some parts of structure.

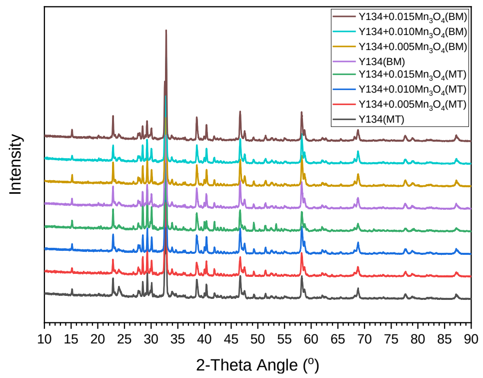

Figure 4 XRD pattern of samples.

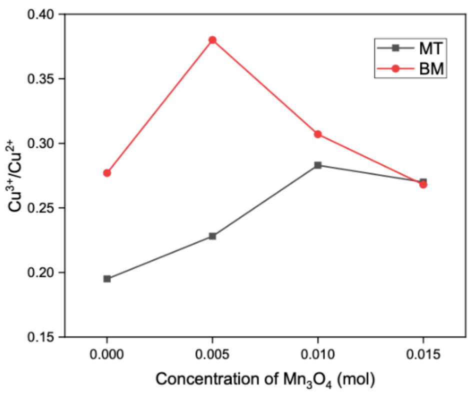

Figure 5 The relation of Cu^{3+}/Cu^{2+} ratio and concentration of Mn_3O_4.

3.5 The resistivity measurement

The critical temperatures of samples obtained from the electrical resistivity measurement were shown in Table 3. and Figure 6. They referred to the relation between temperature in Kelvin unit and electrical resistivity in Ω.m unit represented phase transition temperatures of each sample which hoped fully may increase for room temperature approach. All samples of the Y134 superconductors doped manganese oxide prepared by mortar had assimilative onset transition points at 92.7, 92.3, 92.5 and 91.0 K for 0, 0.005, 0.010 and 0.015 mol of Mn_3O_4 doping with the reverse proportion between normal state resistivity and concentrations of doping. On the other hand, the four samples prepared by ball milling had higher onset critical temperatures at 94.0, 93.0, 95.2 and 98.7 K for 0, 0.005, 0.010 and 0.015 mol of Mn_3O_4 doping, respectively. That showed in Figure 7. They provided the upward trend of critical temperature for amount increasing of Mn_3O_4 doping and agreed with the slight increase of Cu^{3+}/Cu^{2+} ratio in this work and the research of determination of Cu^{2+} and Cu^{3+} by titration in Y134 and Y145 superconductor (8). Moreover, all samples prepared by ball milling in normal state had less resistivity than one from mortar grinding. As a result, the samples prepared by ball milling had higher conductivity than another technique.

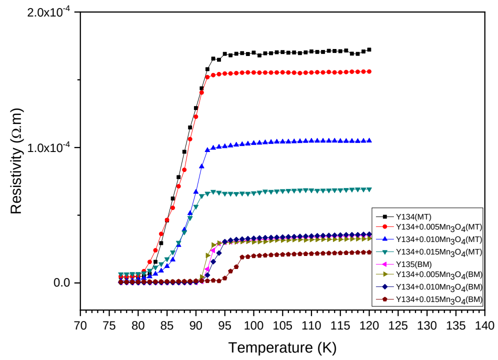

Figure 6 The relation between temperature and resistivity of samples.

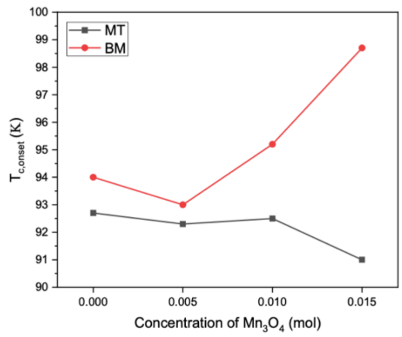

Figure 7 The relation between $T_{c,onset}$ and concentration of Mn_3O_4.

Table 3 Critical temperature of samples.

Samples	Critical temperature (K)			Resistivity at 120 K ($\times 10^{-5}$ Ω.m)
	$T_{c,offset}$	$T_{c,onset}$	ΔT_c	
Y134 (MT)	82.3	92.7	10.4	17.22
Y134 + $0.005Mn_3O_4$ (MT)	82.0	92.3	10.3	15.61
Y134 + $0.010Mn_3O_4$ (MT)	85.0	92.5	7.5	10.49
Y134 + $0.015Mn_3O_4$ (MT)	84.3	91.0	6.7	6.93
Y134 (BM)	91.0	94.0	3.0	3.53
Y134 + $0.005Mn_3O_4$ (BM)	91.0	93.0	2.0	3.28
Y134 + $0.010Mn_3O_4$ (BM)	91.0	95.2	4.2	3.60
Y134 + $0.015Mn_3O_4$ (BM)	94.5	98.7	4.2	2.26

4. Conclusions

We synthesized 2 groups of $YBa_3Cu_4O_{9.5}$ + xMn_3O_4 superconductors; x=0, 0.005, 0.010 and 0.015 via preparation by mortar and ball milling. We found that $YBa_3Cu_4O_{9.5}$ + xMn_3O_4 superconductors prepared by ball milling had more homogeneity than the mortar ones, supported by small standard deviations of grain sizes and stoichiometric ratio from EDX. Moreover, their onset critical temperatures were increased by doping with more concentration of manganese oxide confirmed by the best critical temperature of ball milling sample doped with 0.015 mol of manganese oxide as 98.7 K. It related to Cu^{3+}/Cu^{2+} ratio and average grain size increasing by doping with Mn_3O_4. They probably showed the increase of percentage of superconducting compound. The results of XRD refer to orthorhombic structures for all samples, as showed that the manganese oxide unaffected the main crystal structure of Y134 superconductor agreed with the researches of Mn_3O_4 doping on Y123 superconductor by Salama and co-workers (4-5). However, the Mn_3O_4 doping on Y134 superconductor by using ball milling could reduce porosity, adjoined the grains of Y_{134} superconductor, increased effectiveness of crystallization, and increased the oxygen content in structure by Cu^{3+}/Cu^{2+} ratio analysis that got them had less normal electric resistivity and high critical temperature.

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Declaration of conflicting interests

The authors declared that they have no conflicts of interest in the research, authorship, and this article's publication.

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