# Investigation of Superconductivity and Crystal Structure of Y123, Y358 and Y3-8-11 Prepared by Solid State Reaction and Melt Process

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## Abstract

Pellets of Y123, Y358 and Y3-8-11 were synthesized by solid state reaction and melt process. The Y358 synthesized by solid state reaction showed the highest critical temperature 100 K. The Y123 prepared by solid state reaction showed the highest superconducting phase. Surfaces of solid state reaction sampled were heterogeneous surface and random orientation. The melt samples showed large grain size and homogenous surface. Both samples showed the Y, Ba, Cu and O in the samples without another elements. The solid state reaction samples had higher oxygen content than the melt samples.

*KEYWORDS*: Superconductor; Melt process compound; Solid state reaction

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## Introduction

The first superconducting materials discovered in Lanthanum barium copper oxide in La214 ($La_2BaCuO_4$) with the temperature transition about 35 K. Bednorz and Muller [1] replaced ion of $Y^{3+}$ in $La^{3+}$ the transition increased above 92 K in Y123 ($YBa_2Cu_3O_7$). The Y123 [2] was the first superconducting material that has the critical temperature above boiling liquid nitrogen. The Y123 like was found in Y124 [3] and Y247 [4], which the critical temperature at 80 K and 40 K, respectively. The research in Y family have been intensively studied. A recently synthesized new Y-based compound which the new critical temperature value in Y358 ($Y_3Ba_5Cu_8O_{18}$) [5] has the critical temperature above 100 K. In 2010, Udomsamuthirun et al [6] synthesized a new superconductor under assumption that number Y-atoms plus Ba-atoms is equal to the number of Cu-atoms. The 3-8-11 superconductor showed the highest critical temperature and sharp transition curve. It is now widely accepted that method of the sample preparation have an effect on Y-based superconductor such as magnetic trapping, levitation and increases the critical current density (Jc) [7] and critical magnetic field (Hc) [8] properties,etc. The melt process is an alternative way of preparing of the Y-based superconductor, which first discovered by Jin et al [9]. The main idea of this process is the temperature of the preparing is over the peritectic temperature. The heat treatment decompose the material above at melting temperature. The Y123 had the melting point around 1,030 °C reported Oliveira et al [9]. The heat treatment is used with short time period and then cool down with the very slowly temperature to lower peritectic temperature. The melt process the improved the large grain size of the specimen and presence the secondary phase of Y123 was Y211 which Y211 influenced the flux pinning properties [10], and provide high magnetic field and current density occured in the surface of the specimen.

In this paper, we report a result of Y123, Y358 and Y3-8-11 synthesized by solid state reaction and melt process. Critical temperature (Tc) was investigated by four-probes method and its crystal structure by XRD. Superconducting compound, non-superconducting compound were also investigated and lattice parameters (*a, b, c*) of the two compound were also investigated by Rietveld refinement method [11]. Surface morphology and elementary analysis investigated by SEM and EDX (mapping) techniques. Oxygen content content was carried out by standard iodometric titration method.

## Materials and Methods

Ceramic superconducting samples of Y123, Y358 and Y3-8-11 were synthesized by standard solid state reaction method using raw materials of $Y_2O_3$, $BaCO_3$ and CuO of high purity (99.99%) in desired atomic ratio as 1:2:3, 3:5:8 and 3:8:11. These powders were finely and ground using a mortar and pestle and calcined at 950 °C for period of 15 h in a box furnace in air environment. The calcined powder was reground and recalcined. Black powder was obtained after the second calcinations process. The powder was reground and the hydraulic machine pressed to from 30 mm diameter and 3 mm thick pellets under a pressure of 1500 psi. All pellets were sintered at 950 °C for 24 h and annealed at 500 °C for 12 hrs. The obtained the bulk samples referred to solid state reaction samples(s). For second type, sintered at 950 °C for 12 hours and increase temperature to 1,030 °C for short time period to 30 min and slowly decrease temperature to 950 °C again for 12 hrs. The obtained bulk samples referred to melt samples(m). The used a short is time for melt process to protect bends of the samples. The bending samples cause difficulty in the critical temperature measurement. Crystal structure of the compound were analysed by using the powder X-ray diffraction D8 Advance Discovery diffractometer (high-speed detecter) with CuKα ($\lambda$ = 1.54 Å) radiation at room temperature in the range of 2θ interval 10°-90° and step increment of 0.02° with scan speed of 3.40 degreemin$^{-1}$. The obtained raw data of XRD for refinement with Rietveld method for determined the lattice constant of (*a, b* and *c*), space group and phase composition can be classified to two phases, superconducting phase and non-superconducting phase. Field emission Scanning Electron Microscope (FESEM, FEI Quanta 400) with an accelerating voltage of 20 kV in the secondary image mode and the Energy Dispersive X-ray Spectroscopy (EDXS) was used as the mapping techniques to investigate the surface morphology of the samples. Standard iodometric titration was used to determined oxygen content in the solid state reaction samples and the melt samples. Finally, the samples were characterized and analyzed resistivity by standard four-probes method with current density $3.18\times10^{-3}Am^{-2}$ and the operated temperature ranged from 77 K to 120 K. Electrical lead were attached into the center of samples by silver paste. The electrical resistance of samples at room temperature was in the mΩ range. A thermocouple type K was used as temperature detector.

## Results and Discussion

Electrical resistivity versus temperature of all samples are shown in Fig.1 For Y123, the blue line, black line and light blue line show the transition critical temperatures of samples synthesized by solid state reaction method, respectively. Additionally, the red line, green line and purple line represents the transition critical temperature of the samples synthesized by melt process. When comparison from the curve of the two methods, the samples prepared by solid state reaction show the critical temperature higher than the samples synthesized by melt process method, because the critical temperature measurements were at the surface of the samples. The surface of the samples synthesized by melt process were probably inhomogeneous since sintering temperature above peritectic temperature, thus they showed poor electrical conductivity at surface. On the other hand, the surface of samples synthesized by solid state reaction were more homogenous than samples from melt process, resulting in the better electrical conductivity. The values of the critical temperature of the samples prepared by solid state reaction and melt process are show in the Table 1. The Y358 synthesized by solid state reaction showed the highest critical temperature. The majority of the critical temperature synthesized by solid state reaction show the closely value of critical temperature. Therefore, the heat treatment affected properties of the samples. The solid state reaction may cause more stable crystal structure than the melt process. This result corresponds to the XRD results below.

**Table 1** The critical temperature of our samples.

| Samples | $T_c$onset (K) | |
|---|---|---|
| | solid state reaction (s) | melt process (m) |
| Y123 | 97.01 | 89.99 |
| Y358 | 99.98 | 93 |
| Y3-8-11 | 97.33 | 92 |

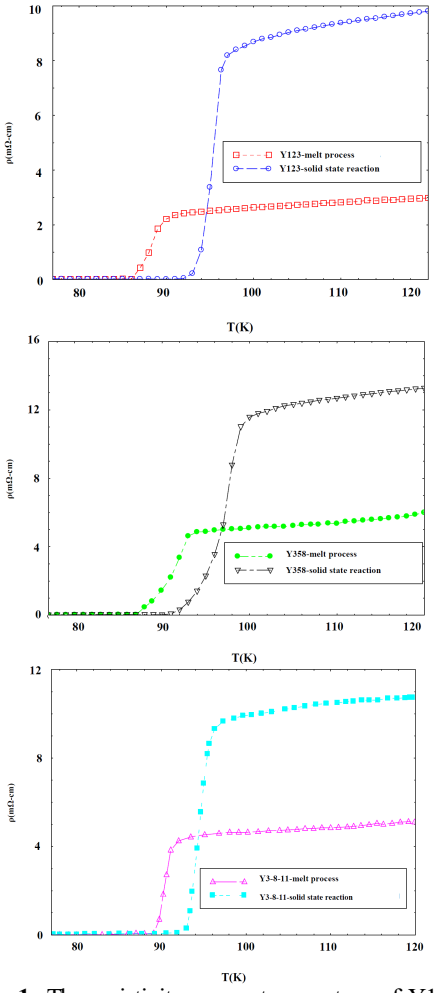


**Fig. 1** The resistivity versus temperature of Y123, Y358 and Y3-8-11 prepared solid state reaction and melt process.

The XRD pattern of all samples are shown in Fig. 2 The characteristic peak showed the polycrystalline and various phases. The main phase of the samples separated in two phases, the superconducting phase and non-superconducting phase as shown in Fig. 3 The blue bar and red bar represent superconducting phase of samples prepared by solid state reaction and the red bar represent the non-superconducting phase, respectively. The superconducting phase had the orthorhombic structure with Pmmm space group. The solid state reaction samples had more superconducting than the melt process samples. The secondary phases was the non-superconducting phase as shown in Fig. 3 The Y211, $BaCuO_2$ and $Ba_2Cu_3O_6$ impurity were found in the samples. The Y211 had is a characteristic phase for Y123. The $BaCuO_2$ and $Ba_2Cu_3O_6$ impurity were found in Y358 and Y3-8-11 samples. The melt process samples had more secondary phase than the solid state reaction samples. The lattice parameters of both phases were characterized from Rietveld refinement as shown in Table 2 and 3 The raw data of the XRD was investigate by using powder X-ray diffraction. The lattice parameters (*a, b* and *c*) and percentage of the phases compound were carried out from Rietveld refinement. The lattice parameter of superconducting phase and non-superconducting phase are shown in Table 2 and 3 The c lattice parameter of prepared solid state reaction was the longer than the melt process samples.

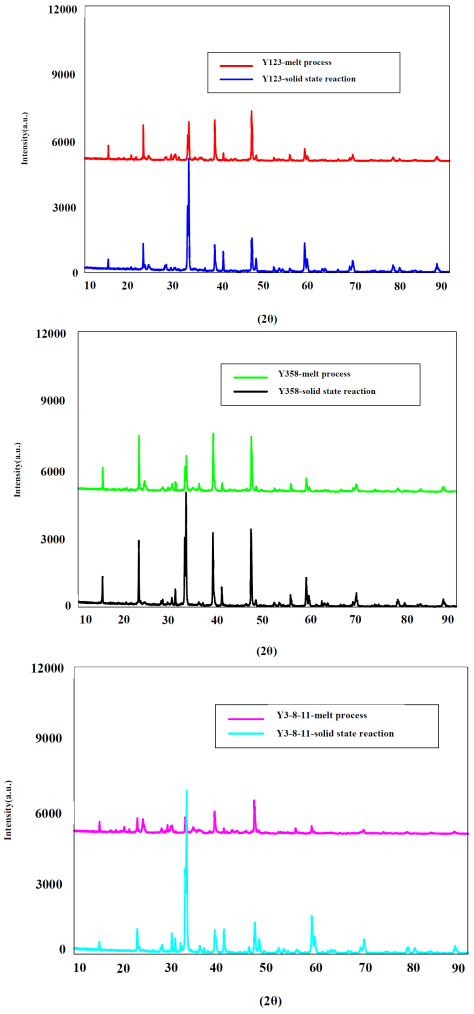


**Fig. 2** The XRD pattern of the prepared solid state reaction and melt process of the Y123, Y358 and Y3-8-11.

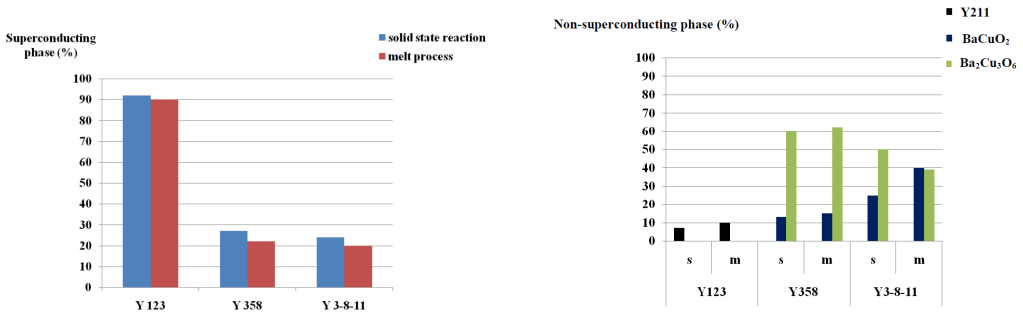


**Fig. 3** Percentage of superconducting phase and non-superconducting phase of the samples.

**Table 2** Lattice parameters of superconducting phase in Pmmm space group.

| Samples | Lattice parameter(Å) | | | *c*/*a* ratio | Anis=200(*b*-*a*)/(*b*+*a*) |
|---|---|---|---|---|---|
| | *a* | *b* | *c* | | |
| Y123(s) | 3.82 | 3.89 | 11.69 | 3.06 | 1.65 |
| Y123(m) | 3.82 | 3.88 | 11.68 | 3.05 | 1.62 |
| Y358(s) | 3.81 | 3.89 | 31.17 | 8.17 | 1.89 |
| Y358(m) | 3.82 | 3.87 | 30.53 | 7.99 | 1.35 |
| Y3-8-11(s) | 3.81 | 3.88 | 42.69 | 11.12 | 1.88 |
| Y3-8-11(m) | 3.82 | 3.88 | 42.11 | 11.03 | 1.55 |

**Table 3** Lattice parameter of non-superconducting phase of our samples.

| samples | Non-superconducting phase | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | Y211, Pbnm(Å) | | | $BaCuO_2$, Im-3m(Å) | | | $Ba_2Cu_3O_6$, Pccm(Å) | | |
| | *a* | *b* | *c* | *a* | *b* | *c* | *a* | *b* | *c* |
| Y123(s) | 7.15 | 12.19 | 5.65 | - | - | - | - | - | - |
| Y123(m) | 7.17 | 12.36 | 5.65 | - | - | - | - | - | - |
| Y358(s) | - | - | - | 18.39 | 18.39 | 18.39 | 13.05 | 20.65 | 11.43 |
| Y358(m) | - | - | - | 18.46 | 18.46 | 18.46 | 13.04 | 20.67 | 11.43 |
| Y3-8-11(s) | - | - | - | 18.38 | 18.38 | 18.38 | 13.04 | 20.58 | 11.41 |
| Y3-811(m) | - | - | - | 18.34 | 18.34 | 18.34 | 13.03 | 20.65 | 11.42 |

SEM (Scanning Electron Microscope) were used to analyzed to microstructure, size and orientation of the samples. The elemental composition of the samples were qualitatively checked by EDX mapping and attached SEM. The SEM micrographs examined on the top view surface at 5,000 magnification. The samples prepared by melt process had more homogenous structure than the solid state reaction samples. Both samples had the random orientation. The EDX mapping analysis found the Y, Ba, Cu and O in both samples without another elements. The oxygen contents(y) of all samples were also determined by using iodometric titration method. The samples prepared by solid state reaction had oxygen content(y) more than the melt process samples. In this result, the most common element in the crystal structure of the samples consist of various oxygen content. It is likely that the samples prepared by solid state reaction may absorb more oxygen from

environment during synthesis than the melt process samples. The oxygen content affect the critical temperature value of the samples corresponding critical temperature measurement. Additionally, the annealed process is important to sample synthesis. The more time of the annealing can be increased the critical temperature possible [12].

**Table 4** The Oxygen content(y) of samples

| Samples | Oxygen content(y) |
|---|---|
| Y123(s) | 6.82 |
| Y123(m) | 6.71 |
| Y358(s) | 18.00 |
| Y358(m) | 17.72 |
| Y3-8-11(s) | 24.43 |
| Y3-8-11(m) | 24.06 |

## Conclusion

The bulk ceramics superconducting materials of Y123, Y358 and Y3-8-11 were synthesized by solid state reaction and melt process. The $T_c$ onset, crystal structure and phases composition, surface morphology, elementary analysis and oxygen content were investigated by four-probes measurement, XRD, SEM, EDX and iodometric titration method, respectively. The samples synthesized by solid state reaction method showed higher critical temperature than the samples prepared melt process method. The samples compose of both superconducting phase and non-superconducting phase. The lattice parameters were characterized by the Rietveld refinement method. The solid state reaction samples showed higher superconducting phase in Y123. The surface of solid state reaction samples were heterogeneous with random orientation. The melt samples showed the large grain size and homogenous surface. The EDX mapping analysis showed the Y, Ba, Cu and O in the both samples and without another elements. The solid state reaction samples contained higher oxygen content than the melt samples.

## References

[1] J.G. Bednorz, K.A. Muller, Possible High $T_c$ Superconductivity in the Ba-La-Cu-O System, Z.Phy.B. 64 (1986) 189 – 193.

[2] K. Wu, J.R. Ashburn, C.J. Torng, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.Q. Wang, C.W. Chu, Superconductivity at 93 K in a New Mixed-Phase Y-Ba-Cu-O Compound System at Ambient Pressure, Phys. Rev. Lett. 58 (1987) 908 – 910.

[3] P. Marsh, R.M. Fleming, M.L. Mandich, A.M. Desantolo, J. Kwo, M. Hong, L.J. Martinez- Miranda, Crystal Structure of the 80 K Superconductor $YBa_2Cu_4O_8$. Nature.334 (1988) 141–143.

[4] P. Bordet, C. Chaillout, J. Chenavas, J.L. Hodeau, M. Marezio, J. Karpinski, E. Kaldis, Structure Determination of the New High Temperature Superconductor $Y_2Ba_4Cu_7O_{14+x}$, Nature. 334 (1988) 596 – 598.

[5] A. Alibadi, Y.A. Farschi, M. Akhavan, A new Y-based HTSC with Tc Above 100 K, Physica C. 469 (2009) 2012 – 2014.

[6] P. Udomsamuthirun, T. Kruaehong, T. Nilkamjon, S. Ratreng, The New Superconductors of YBaCuO Materials, J. Supercond. Nov. Magn. 23 (2010) 1377 – 1380.

[7] T. Goto, Critical current density of filamentary Y 123 superconductor, Physica C. 263 (1996) 450 – 452.

[8] S. Seiki, A. Hayashi, H. Okamoto, T. Izumi, Y. Shiohara, Critical current properties in magnetic fields of YBCO superconducting rods prepared by unidirectional solidification method, Physica C. 412 – 414 (2004) 963 – 966.

[9] C.J.V. Oliveira, A.D. Bortolozo, B. Ferreira, C.A.M. dos Santos, A.J.S. Machado, Effect of $Ta_2O_5$ addition on the texture of the Y123 superconductor, Physica C. 422 (2005) 83 – 87.

[10] J. Mucha, K. Rogacki, H. Misiorek, A. Jezowski, A. Wisniewski, R. Puzniak. Influence of the Y211 phase on anisotropic transport properties and vortex dynamics of the melt-textured Y123/Y211 composites, Physica C. 470 (2010) S1009 – S1010.

[11] J. Carvajal, An Introduction to the program FULLPROF, Laboratoire Leon Brillouin first ed, 2001.

[12] X. Chauda, T. Prikhna, Y. Savchuk, A. Joulainc, E. Haanappel, P. Diko, L. Porcar, M.Soliman, Improved magnetic trapped field in thin-wall YBCO single-domain samples by high-pressure oxygen annealing, Mat. Sci. Eng. B. 151 (2008) 53–59.