Ferromagnetism in 2212 Phase Bi-Sr-Ca-Cu-O Nano-Superconductors

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Abstract- *Superconductors are characterized by zero resistance and Meissner effect. At below critical temperature (Tc), these materials exhibit diamagnetic properties. On the other hand, materials in nano-crystal size have specific properties that differ from bulk state. Nanomaterials are characterized by surface effect which influences physical and chemical properties of the materials. Combining these two mayor fields, it can be obtained superconductors in nano-crystal size (below 200 nm) using simple method (called as nano-superconductors). Generally, ceramic-oxides in nano-crystal size, even in cuprate-superconductors, may have ferromagnetic behavior at room temperature. In this research, Bi and Bi,Pb- based nano-superconductors synthesized by wet mixing technique have Tc □80 K for 2212 (Bi2Sr2CaCu2O8-□ and Bi1,6Pb0,4Sr2CaCu2O8-□) phases. They also exhibit ferromagnetism effect and hysteresis curve although at well above Tc. This is unusual phenomenon because superconductor materials are generally diamagnetic at below Tc and paramagnetic at normal state. This phenomenon is possibly due to magnetic moments which may possibly come from oxygen vacancies of the nanoparticles surface.*

Keywords- BSCCO, Superconductors, nanomaterials, ferromagnetism

I. INTRODUCTION

Superconductor system of Bi-Sr-Ca-Cu-O (BSCCO) has been investigated intensively by many investigators. BSCCO systems relatively have high critical temperature (Tc). The Tc of this family superconductor is to be found has oxygen stoichiometry dependency. The role of oxygen stoichiometry on the superconductivity of these systems is not yet as well understood. Sample processing conditions such as raw material variation, synthesis method, annealing temperature, annealing time, cooling rate, atmosphere/gaseous environment can all have effect on the crystal structure and hence affect Tc. Among the three superconducting phase of Bi-system, Bi-2212 ($Bi_2Sr_2CaCu_2O_x$) is highly stable and has critical temperature close to 85 K [1].

Many kinds of raw materials and synthesis techniques have been used to synthesis this superconductor system. Several methods to synthesis Bi-based superconductor are solid state reaction,

Floating Zone (FZ) method, self-flux method, Travelling Solvent Floating Zone (TSFZ) method [2,3]. Generally, these kinds of methods result superconductor both powder and/or bulk in micrometer crystal size (□ 200 nm). This paper attempts to obtain Bi-based superconductors in nanometer crystal size using simple synthesis techniques. As known that the smaller crystal size, the larger surface area, so it may change and/or improve physical properties, such as electrical and magnetic properties, of the materials.

Nano-structured superconductors have been investigated intensively in recent year. Kato, et.al. [4] have investigated the superconducting state of the nano-sized anisotropic superconductors. Investigation of surface magnetism in nano-scale particles was performed by several researchers [5,6]. The properties of ferromagnetic superconductors have been also investigated [7]. Rao,et.al groups [8,9] shows that several non-magnetic materials and superconductor materials (such as YBCO) having crystal size below 200 nm exhibit ferromagnetism behavior at Tc and also at room temperature. These phenomena are showed by hysteresis curve of YBCO and NbN superconductor in different temperature and sample form. This research tries to investigate the unusual magnetic properties of Bi-2212 and (Bi,Pb)- 2212 nano-structure superconductors.

II. EXPERIMENTAL

Raw materials used in this research are Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO to form Bi-2212 and Bi-2223. PbO_2 is used as dopant to form (Bi,Pb)-2212 and 2223 with x=0.4. All reagents are from Merck with PA grade. Acid solution for dissolvent is HNO_3.

Each of raw materials (Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO) with ratio 2:2:1:2 (Bi-2212) is dissolved by HNO_3 for wet mixing procedure. The resulted solutions are mix together with hot plate magnetic stirrer at 70°C until homogeny (without any precipitation). It is continued by heating process at 100 – 200°C until it will form crust-like precipitation. The precursor is calcinated at 780ºC for 3 hours and then sintered at 825ºC with variation of holding time (1 – 8 hours) to control crystal size of Bi-based nano superconductor. The sintering process is applied in step by step (cycling in every 1 hour).

X ray diffraction (XRD) is conducted to investigate crystal structure of the nano- superconductors. Analyzing peak intensities and their FWHM of data diffraction is to investigate average composition and crystal size in materials respectively. Transmission Electron Microscopy (TEM) is applied to observe nano-structure of superconductor's particles. Superconducting Quantum Interference Device (SQUID) is used to study the critical temperature (Tc) and hysteresis curve of the superconductor powders.

III. RESULT AND DISCUSSION

XRD is used to analyze 2212 superconductor phases that may form for all synthesized samples. Figure 1 (a) and (b) shows two examples of XRD patterns. All of nano-superconductor samples are obtained by a simple wet mixing method with a short and relatively low temperature. The goal of this treatment is to keep crystal size in nanometer size (below 200 nm). As can be seen that phase growth of (Bi,Pb)-2212 is faster than Bi-2212 sample. It is showed in Figure 2. This may be caused by Pb melting when sintering process that can facilitate diffusion process for all atoms to combine and react to form much more 2212 phases. From the XRD results it can be noticed that the volume fraction of Bi2212 and (Bi,Pb)-2212 phases increase with increasing the sintering time up to 8 hours. The volume fractions of Bi-2212 and (Bi,Pb)-2212 phases for all the samples are given in Figure 2. The longer sintering time will give chance for materials to grow and also causes increasing crystal size.

It's difficult to grow pure 2212 crystals reproducibly due to the incongruent character of its melting precipitation rate of each raw materials and growth mechanism complexity of the 2212 with other cuprate superconductors such as $Bi_2Sr_2CuO_z$ (2201) or precipitation of other impurities. Impurities phases in synthesized sample as shown in Figure 1 include Bi-2201, $CaCO_3$, and CuO. These phases are due to relatively low sintering time that affects imperfection of all raw materials to react with the others.

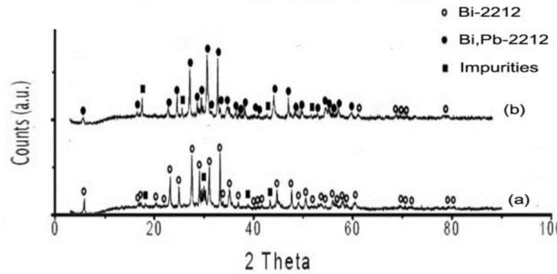


FIGURE 1. XRD pattern of synthesized samples with different sintering time: (a) Bi-2212 for 8 hours and (b) (Bi,Pb)-2212 for 4 hours

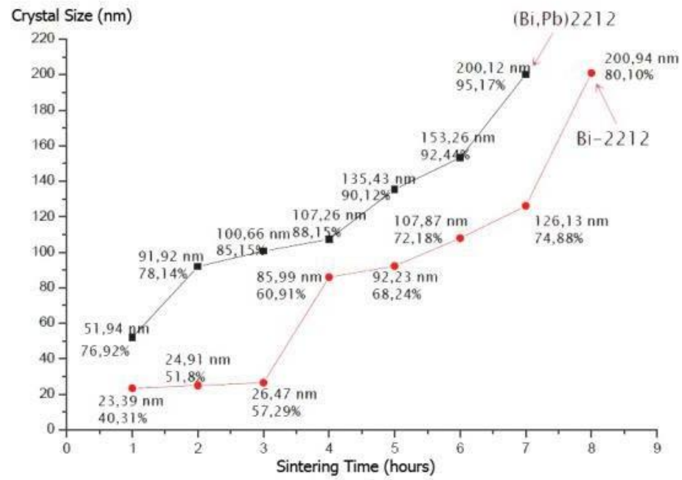
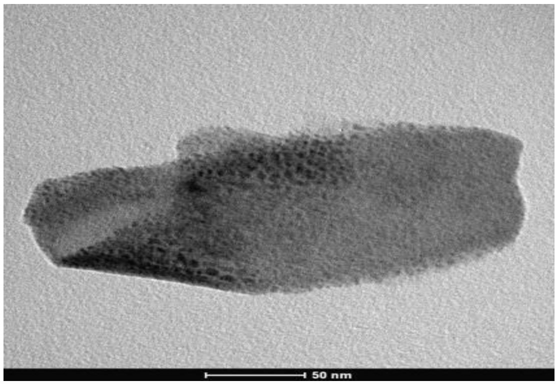
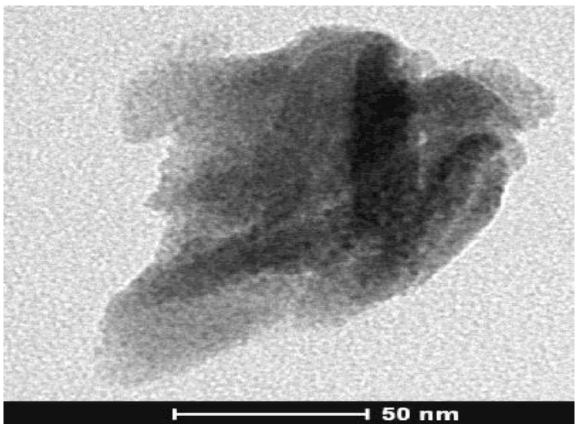


FIGURE 2. Effect of sintering time to crystal size of both synthesized 2212 phases, analyzed from XRD spectra for all synthesized nano-superconductors (including XRD pattern of Figure 1)

Average crystal size obtained in Figure 2 for all samples is calculated using Scherrer equation for several peaks that identified as Bi-2212 phase. Using cycling sintering process in every 1 hour, as expected, all samples have crystal size below □200 nm. For verification of the nano-crystallization of synthesized samples, it is necessary to have TEM observation. Figure 3 (a) and (b) are TEM images for Bi-2212 at 8 hours sintering time and (Bi,Pb)-2212 at 4 hours sintering time respectively. According to these two TEM images, it is proved that calculated crystal size (Figure 2) is approximately similar to TEM observations for the corresponding samples. It means that nano-crystallization takes place in formation of superconducting phases. Based on these two images, it can be seen that average crystal size of each samples was definitely in nanometer scale.



(a)



(b)

FIGURE 3. Particle morphology of synthesized samples with different sintering time: (a) Bi-2212 for 8 hours (particle size □200 nm) and (b) (Bi,Pb)-2212 for 4 hours (particle size □100 nm)

Critical Temperature (Tc) and magnetization (M- H) measurement of sample Bi-2212 with sintering time for 8 hours and (Bi,Pb)-2212 with sintering time for 4 hours had been conducted using SQUID. Figure 4 shows that Tc offset of the Bi-2212 and (Bi,Pb)- 2212 is almost the same, that is Tc = □80 K. This is evidence that even materials in nanosize particles, they still have almost the same properties in case of Tc value [10]. Figure 4 can also give information that the materials behave as diamagnetic materials at superconducting state.

Magnetization curve of Bi-2212 with sintering time for 8 hours and (Bi,Pb)-2212 with sintering time for 4 hours in external magnetic field at Tc point (80 K) and room temperature (300 K) is shown in Figure 5 (a) and (b) respectively. According to Figure 2, these two samples have average crystal size □200 nm and □100 nm respectively. Magnetization at Tc and room temperature shows hysteresis loops which come out because of magnetic moments arising from the oxygen vacancies at the surfaces of the nanoparticles [9]. Figure 5 (a) shows more clearly hysteretic behavior than Figure 5 (b). This may be due to the presence of Pb-doped that affects overall magnetic moments. The mechanism of this phenomenon has not understood yet.

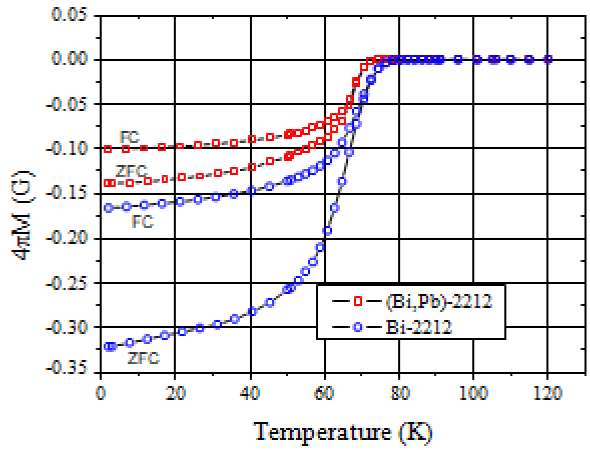
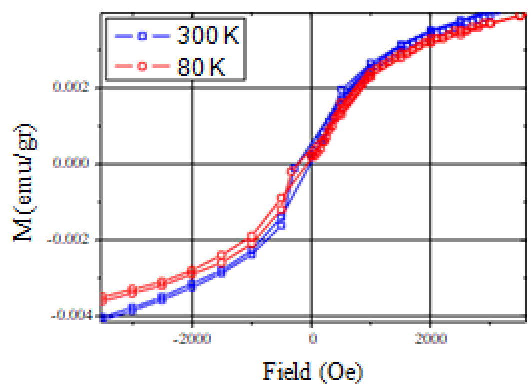
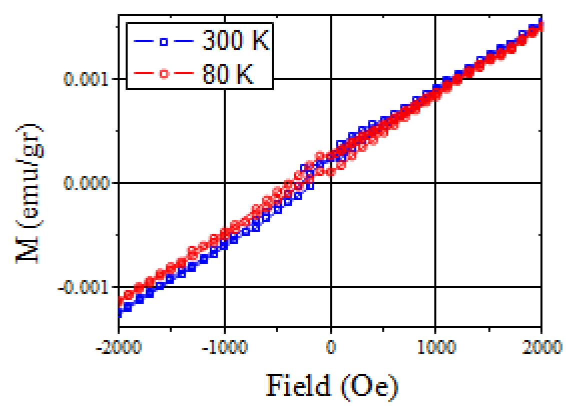


FIGURE 4. Tc of sample Bi-2212 with sintering time for 8 hours and (Bi,Pb)-2212 with sintering time for 4 hours



(a)



(b)

FIGURE 5. M(H) curve at 80 K and 300 K for sample (a) Bi-2212 with 8 hours sintering time (□200 nm); (b) (Bi,Pb)- 2212 with 4 hours sintering time (□100 nm).

IV. CONCLUSION

Synthesis of Bi-2212 and (Bi,Pb)-2212 superconductors using simple wet mixing method has succeeded to form dominant superconducting phases. These materials have critical temperature approximately 80 K. From XRD analysis, the samples have nanocrystal size. In magnetization consideration, they behave like as ferromagnetic materials even at Tc and room temperature due to magnetic moments arising from the oxygen vacancies at the surfaces of the nanoparticles.

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