ISSN 2229-5518

Magnetic Susceptibility of Superconducting MgB_2 Nanomaterials

Reynante C. Embalzado, Gil Nonato C. Santos

Abstract — Superconducting MgB_2 nanomaterials were synthesized using the Horizontal Vapor Phase Crystal Growth (HVPCG) technique with growth temperatures of 900℃, 1000℃, 1100℃ and 1200℃ with heating time of 2 to 12 hours with a two- hour increment. The grown structures were characterized by its surface morphology, crystal structure and critical temperature. Results revealed that the critical temperature of MgB_2 nanomaterials fabricated at 1000°C was at 33K. SEM images revealed nanomaterials of different structures such as nanowires, nanobelts, nanorods and nanoparticles. Crystal structure of the synthesized materials revealed that the nanomaterials have growth orientation of (100), (101), and (110), which indicated that the synthesized structures are polycrystalline.

Index Terms— Nanomaterials, Horizontal Vapor Phase Crystal Growth, Superconducting, Magnetic Susceptibiility

1 Introduction

The studies of the MgB_2 and its derivative have been focused on the bulk, thin films, and wires. Those forms of materials can be productively synthesized with well-established techniques and their commercial products have been successfully manufactured. Since the discovery of carbon nanotubes in 1991, the worldwide nanotechnology research has been extended to space-restrained physical phenomena. Fabrication and investigation of nanoscale devices of MgB_2 provide the fundamental understanding of the effect of dimensionality and size on superconductivity. MgB_2 is a promising superconductor for practical applications in the field of superconducting magnets for MRI, due to its high *Tc* and relatively low material costs. The development of tapes and wires was much faster than for many others HTS and LTS materials and commercial wires and tapes became available only a few years after its discovery. There have been limited reports on the fabrication of MgB_2 nanomaterials. Most of the synthesis methods used to grow MgB_2 nanomaterials are multi-steps. Lai et al [1] fabricated MgB_2 nanowires using vapor transport and reaction process, Zhao et al [4] synthesized nanowires through reactive sintering, Zhou et al [5] fabricated MgB_2 tubelike nanostructures using thermal evaporation of MgB_2 particles precursors. The other synthesis methods to grow MgB_2 nanowires are the direct pyrolysis from MgB_2 nanoparticles [6] or the pyrolysis from the mixed gel in the diborane-N_2 atmosphere [7]. The purpose of the study is to synthesize and characterize Magnesium Diboride (MgB_2) nanomaterials using horizontal vapor phase crystal growth technique. The study also aims to investigate the optimum growth parameters on fabricating nanomaterials. The effect of nanoscale crystal size on the superconducting property of Magnesium Diboride will be examined.

- *Reynante Embalzado, Master of Science in Physics, De La Salle University -Manila Philippines, E-mail:*
- *Gil Nonato C. Santos, Doctor of Philosophy in Materials Science and Engineering, De La Salle University-Manila, Philippines. E-mail: santosg@dlsu.edu.ph*

2 Experimental Section

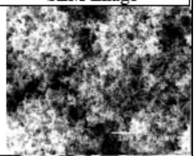
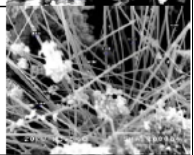
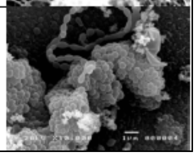
2.1 Synthesis of MgB_2 Nanomaterials

Thirty-five milligrams (35mg) of Magnesium Diboride powder from Accumet Materials Co. was used and loaded into a clean quartz tube and was sealed at one end. The tube was then connected to a high vacuum system and sealed at 10^{-6} Torr. The tube was then heated in the horizontal tube furnace with varying temperature of 900°C, 1000°C, 1100°C and 1200°C with growth times of 2, 4, 6, 8, 10 and 12 hours and with constant ramp time of 80 minutes. The tube was then allowed to cool down to room temperature, after which it was opened for investigation. The grown materials were then characterized using the scanning electron microscope, X-ray dispersive spectroscopy and the HALL apparatus.

3 Results and Discussion

It was observed that varying the growth parameters resulted to the formation of different nanostructures which include nanowires, nanobelts, nanorods, nanosheets and nanochains, with nanowires as the dominant structures. Table 1 shows the optimum growth parameters of each nanostructure. For the as-synthesized material, the dominant peak from (101) plane can be observed while weaker diffraction peaks are seen from (100) and (110) planes. This polycrystalline nature of the material can be verified from the SEM images. The miller indices of the dominant MgB_2 peaks correspond to a hexagonal crystal structure with lattice parameters of *a* and *c* – axes of 3.085 Å and 3.524 Å, respectively, which is identical that of the bulk sample. The impurities MgO and MgB_4 are also observed in the synthesized material and their intensities seemed to increase. The additional MgO and MgB_4 could be the result of the reaction of the trapped oxygen in the quartz tube during heating.

Table 1. Optimum Growth parameters for MgB_2 nanomaterials

Nanostructure	Growth Parameters	SEM Image
Nanowire	Growth Temperature = 1 200°C Heating Time = 8 hours Ramp Rate = 14.6 °C/min	
Nanosheet	Growth Temperature = 1 100°C Heating Time = 12 hours Ramp Rate = 13.4 °C/min	
Nanorod	Growth Temperature = 1 200°C Heating Time = 8 hours Ramp Rate = 14.6 °C/min	
Nanosphere	Growth Temperature = 1 200°C Heating Time = 10 hours Ramp Rate = 14.6 °C/min	

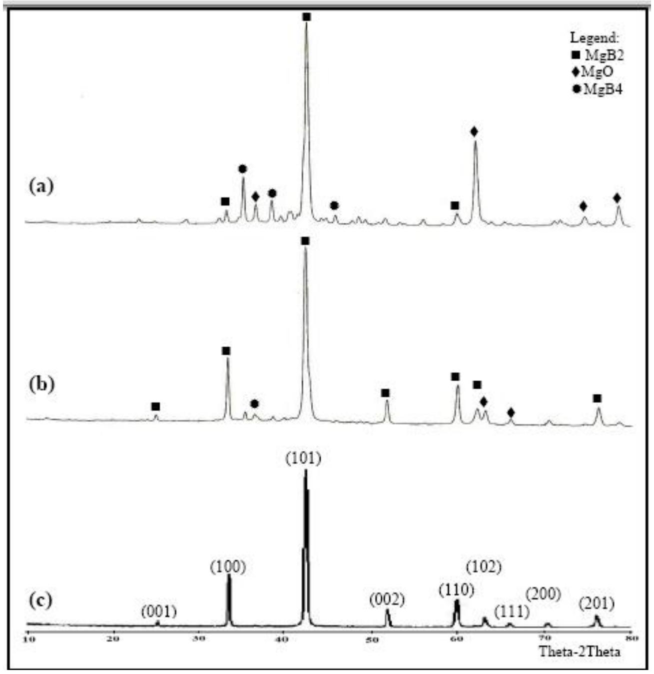


Figure 1. X-ray diffraction patterns of the (a) synthesized nanomaterial, (b) initial sample and (c) high purity powder.

The ρ-T curve of the synthesized material is shown in Figure 2b. The nanomaterial displays semiconductor behavior, the same with the bulk counterpart. The zero resistance transition temperature deduced from the measurement is 13K with an onset temperature of 33K, which is lower compared to their bulk counterparts. The rough curve could be the result of the additional MgO present in the sample. EDX test showed that the oxygen content in the fabricated material has increased by a certain amount. This was obtained during the heating process where the sample reacted with the oxygen that was trapped in the quartz tube during sealing. The low *Tc* (33K) of the nanomaterial was due to the increase of the grain boundaries of the material which resulted to less connectivity and more resistance. This result is consistent as reported in the literature, where the decrease in the crystal size of MgB_2 resulted to the decrease in its critical temperature. The result suggests that the critical temperature of MgB_2 superconductor depends on its grain size. The smaller the grains are, the lesser the critical temperature. By changing the grain size to nanoscale the *Tc* has reduced by 1K. Materials synthesized at heating temperature at 1100°C and 1200°C did not show superconductivity, instead the materials became insulator. This is due to the increase of impurities present in the material.

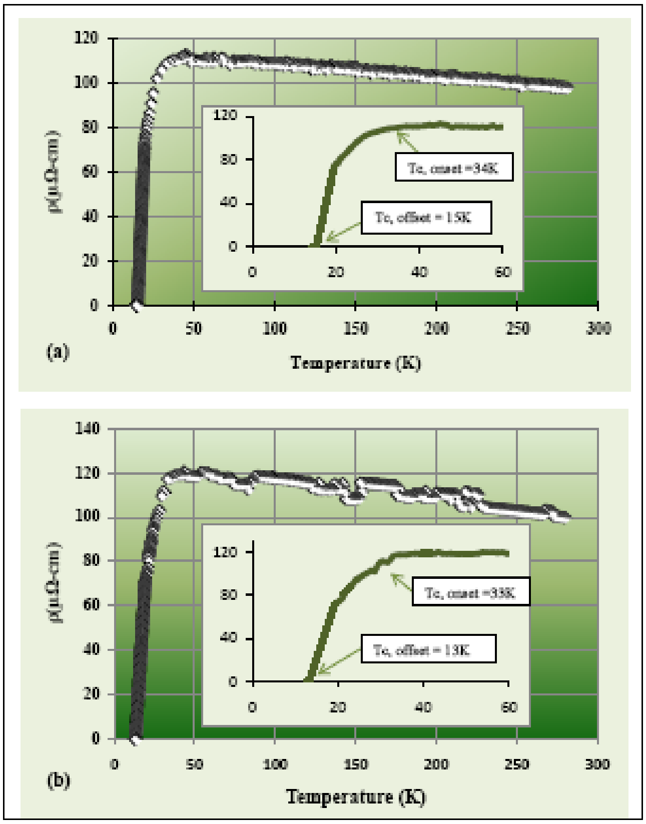


Figure 2. The resistance versus temperature curves of (a) bulk sample and (b) nanomaterials fabricated at 1000°C in 6h.

4 Conclusion

In this study, Magnesium Diboride nanomaterials were fabricated using Horizontal Vapor Phase Crystal Growth method. SEM characterization revealed nanomaterials of

ISSN 2229-5518

different sizes are grown inside the quartz tube. In a 900°C heating temperature, unreacted magnesium diboride powder was observed and no nanomaterial was formed. When the temperature was increased to 1000°C, some microstructures particularly microspheres were observed. At higher temperatures most especially, more nanostructure materials were observed. Dense and tangled nanowires are predominantly observed on higher heating times. These nanowires are several micrometers in length and 60 -170 nm in diameter. The diameter, moreover, seems to correlate the heating time, therefore, more heating time resulted in thinner diameters of MgB_2 nanowires. XRD patterns of the synthesized material reveal dominant MgB_2 phase and trace amounts of impurity phases. Miller indices are indicated in each peak. The diffraction peaks of (100), (110), and (110) correspond to MgB_2 hexagonal structures with calculated parameters of *a* and *c* –axes of 3.085 Å and 3.524, respectively, which is a match with the bulk sample. The presence of the impurity is most likely due to the reaction of the initial material with the air atmosphere. In addition, during heating, the trapped oxygen in the quartz tube reacted with the powder, thus, producing MgO and MgB_4. Electrical resistivity of the fabricated nanomaterials at 1000°C was measured using four-point probe method. The result shows that the critical temperature of the synthesized material is 33K which is below the *Tc* of the bulk counterpart. The transition width is 20K, which is very broad. The low critical temperature of the material is due to the increase of the grain boundaries of the sample which resulted to less connectivity and more resistance. The broadened transition width is indicative of large amount of defects and impurities within the sample. Materials synthesized at heating temperature of 1 100°C and 1 200°C did not show superconductivity, due to the increase of impurities present in the material. The findings suggest that the optimum growth parameters are 12 hours and 1 200°C. More nanomaterials are grown in the heating time of 12 hours and growth temperature of 1 200°C such as nanowires, nanorods and nanobelts. The study shows that the growth temperature is vital to control the size and number of the nanostructures. The higher the temperature, the more materials sublimed and traveled in the colder region of the quartz tube that resulted to the formation of more nanomaterials. The XRD test shows that the crystal structure of the fabricated material is hexagonal, which is the same with the initial material. Four-point resistivity measurements imply that the nanomaterials are still superconductors. However, the critical temperature has decreased by 1K. This is because of the size dependence of Tc of the superconducting material. The smaller the crystal size of MgB_2 powder, the lower its Tc.

5 Recommendation

Further characterization should be done on the materials synthesized by this method such as the hall mobility, magnetic susceptibility, critical current density and critical field. It is also recommended the use high resolution imaging so as to fully investigate the surface morphology and growth mechanism of the synthesized materials. It is also proposed the use of Energy Dispersive X-ray (EDX) that can quantify Boron element so as to study the effect of varying growth time and temperature on the stoichiometric composition of the synthesized materials.

References

[1] Lai, S.H., Liu,S.C., Lan, M.D. (2007). Fabrication of MgB2 Nanowire and its Superconductivity, *Journal of Crystal Growth*, *304*, 460-463.

[2] Zhao, Q., Liu, Y. C., Shi, Q., Gao, Z. (2007). Characteristic and synthesis mechanism of MgB2 nanoparticles in solid-state reactive sintering. *Physica C 467*, 145-149.

[3] Zhou, S. M., Wang, P., Li, S., Zhang, B., Gong, H. C., Zang, X. T. (2009). Superconducting Single Crystalline MgB2 Nanotubes, *Materials Letters*, 1680-1682.

[4] Bando, Ma. R., Mori, T., Golberg, D. 2003. Direct Pyrolysis Method for Superconducting Crystalline MgB2 Nanowires, *Chemical Materials, 15 (16)*, 3194–3197.

[5] Nath, M., Parkinson, B.A. (2006). A simple Sol-Gel Synthesis of Superconducting MgB2 Nanowires, *Advanced Materials, 18*, 1865-1868.

[6] Glowacki, B.A., Majoros, M., Vickers, M., Evetts, J.E., Shi, Y. and McDougall, I. 2001. Superconductivity of Powder-In-Tube MgB2 Wires, *Superconductor Science and Technology, 14*, 193.

[7] Cui,C., Liu, D., Shen, Y., Sun, J., Meng, F., Wang, R., Liu, S., Greer, A.L., Chen, S., Glowacki, A.B. (2004). Nanoparticles of the superconductor MgB2: structural characterization and in situ study of synthesis kinetics. *Acta Materialia, 52*, 5757-5760.

[8] Park, S.C., Chung, J.K., Lim, Y. J., Kang, S.G., Song, K.J., Kim, C.J. 2008. Synthesis and characterization of nano-sized MgB2 powder by spray pyrolysis method, *Physica C, 468*, 1817-1820.

[9] Yang, C.C., Li, S.(2007). Size Dependence of Critical Transition Temperature of MgB2. Proceedings 31st Annual Condensed Matter and Materials Meeting.

[10] Varin, R.A., and Chiu, C. 2006. Synthesis of nanocrystalline magnesium diboride (MgB2) metallic superconductor by mechano-chemical reaction and post-annealing. *Journal of Alloys and Compounds, 407*, 268–273.