การสังเคราะห์วัสดุอะมอร์ฟัสของ BSCCO ด้วยวิธี melt-quench

Synthesis of BSCCO amorphous materials by melt-quenched method

Presented in The 2nd Progress in Advanced Materials: Micro/Nano Meterials and Applications

*ทศวรรษ สีตะวัน (Tosawat Seetawan)**

บทคัดย่อ

วัสดุอะมอร์ฟัส $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+d}$ (BSCCO, x = 1, 2, และ 3) สังเคราะห์ด้วยวิธีการหลอมแล้วทำให้เย็นตัวลงอย่างรวดเร็วแล้วทำการสังเกตและวัดสมบัติเชิงกล สังเกตลักษณะโครงสร้างระดับจุลภาคด้วยกล้องจุลทรรศน์อิเล็กตรอนแบบสแกนนิง (SEM) วัดและออกแบบโครงสร้างผลึกด้วยเครื่องเลี้ยวเบนของรังสีเอกซ์ (XRD) และโปรแกรม Visualization of Crystal Structure (VICS) ตามลำดับ วัดและคำนวณสมบัติการยืดหยุ่นด้วยเครื่องวัดความเร็วเสียงแบบอัลทราโซนิกและวัดความแข็งระดับจุลภาคด้วยเครื่องทดสอบความแข็งระดับจุลภาคตามลำดับ ผลการวิจัยพบว่า สามารถสังเคราะห์วัสดุอะมอร์ฟัส BSCCO ได้ทั้ง 3 เฟส คือ $Bi_2Sr_2CuO_6$ (Bi-2201), $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) และ $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) ยืนยันจากผลการวัดและวิเคราะห์ของ XRD และคำนวณด้วยโปรแกรม Powder Cell มีสมบัติการยืดหยุ่นที่ดี เช่น บัลก์มอดุลัส (K), มอดุลัสของยัง (E), เชียร์มอดุลัส (G) และมีสมบัติความแข็งแบบวิกเกอร์ (H_V) เหมาะสมกับสมบัติพื้นฐานที่ดีของวัสดุเทอร์โมอิเล็กทริก

Abstract

$Bi_2Sr_2Ca_{x-1}Cu_xO_{6+d}$ (BSCCO, x = 1, 2, and 3) amorphous materials have been synthesized by melt-quenched method and the mechanical properties can be measured. The microstructures of amorphous materials can be observed by the scanning electron microscope (SEM). The crystal structures of the glasses can be measured and simulated by x-ray diffraction (XRD) technique and visualization of crystal structure (VICS) software, respectively. The elastically properties and Vickers hardness are measured and evaluated by ultrasonic sound velocity measuring device and micro-hardness tester, respectively. It found that, the BSCCO amorphous materials are composed of $Bi_2Sr_2CuO_6$ (Bi-2201), $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) and $Bi_2Sr_2Ca_2Cu_3O_{10}$ (Bi-2223) phases, these phases confirmed by the XRD analysis and calculated by Powder Cell software. The amorphous materials have been a good elastic value of bulk modulus(K) Young's modulus(E), shear modulus (G) and Vickers hardness(H_V), these properties are corresponded to a good thermoelectric materials.

คำสำคัญ: สารตัวนำยวดยิ่ง BSCCO, วัสดุอะมอร์ฟัส, สมบัติเชิงกล, วัสดุเทอร์โมอิเล็กทริก

Keywords: BSCCO superconductors, amorphous materials, mechanical properties, thermoelectric materials

Program of Physics, Sakon Nakhon Rajabhat University, Muang District, Sakon Nakhon Province 47000, Thailand.

**Corresponding author, E-mail: t_seetawan@mail.snru.ac.th*

1. Introduction

The amorphous materials for superconductors like $Bi_2Sr_2CuO_6$ (Bi-2201), $Bi_2Sr_2CaCu_2O_8$ (Bi-2212) and $Bi_2Sr_2Ca_2Cu_2O_{10}$ (Bi-2223) phases are several application studies. Therefore, developmental investigations of the various mechanical properties of amorphous materials or glass ceramics phases are very important of applicable thermoelectricity. The superconductivity of Bi-2201, Bi-2212, and Bi-2223 bulk samples have the critical temperature (T_C) of 10 K, 85 K and 110 K, respectively (Maeda H. et al., 1988). The C lattice parameters for three phases are 2.46, 3.06, and 3.71 nm, respectively (Terascon J.M. et al., 1988).

Furthermore, Seebeck coefficient (S) for BSCCO thermoelectric materials are either positive or negative depending on the chemical compositions, substitutional some materials, and preparative conditions (Aksan M.A. and Yakinci M.E., 2004), (Chatterjee S. et al., 1996), (Chatterjee S. et al., 1998). The study of thermoelectric properties of BSCCO glass ceramics would be important to measurement.

The paper is to synthesis the $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+\delta}$ (x = 1, 2, and 3) amorphous materials by melt-quenched method. Furthermore, mechanical properties of the amorphous materials have also been measurement and evaluation for prediction the thermal conductivity.

2. Experimental

The $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+\delta}$ (x = 1, 2, and 3) amorphous materials are prepared by the melt-quenched method (Seetawan T., 1998), (Som K.K. and Chaudhuri B.K., 1990). The Bi_2O_3, $SrCO_3$, $CaCO_3$, and Cu_2O initial powders are high purity (99.99%) and mixed in an agate mortar for 2 h. The mixture was melted in an α-alumina crucible at 1,200 ^oC for 30 min. Molten mixture was quickly poured onto a cold copper plate box and pressed with another cold copper plate to obtain rapidly quenched amorphous materials. The as quenched amorphous materials are analyzed by x-ray diffraction (XRD) and the XRD patterns are calculated by using Powder Cell software. The morphologies of the as quenched amorphous materials are observed by scanning electron microscope (SEM). The densities (d) of the as quenched amorphous materials are determined from the measured weight and dimensions. The longitudinal and shear sound velocities of amorphous materials are measured by an ultrasonic pulse-echo method to evaluate the shear modulus (G), Young's modulus (E) and Debye temperature (Θ). The Vickers hardness (H_V) of amorphous materials are measured by a micro-hardness tester. The thermal conductivity (κ) of amorphous materials are predicted from the Debye temperature values.

3. Results and discussion

3.1. Amorphous materials preparation

The as quenched amorphous materials are the large size of 20 x 20 x 5 mm^3, the face of glasses are sparkle like a precious as shown in Figure 1, indicate ceramic or amorphous behavior. It might be due to a good thermoelectricity for low thermal conductivity. In fact, the glasses have even lower thermal conductivity compared with crystalline materials because the amorphous structure scatters phonons to mean-free paths of atomic dimensions. Thus the ideal thermoelectric material resembled a "phonon glass and an electron crystal" (Slack G.A., 1995), (Sales B.C., 1998).

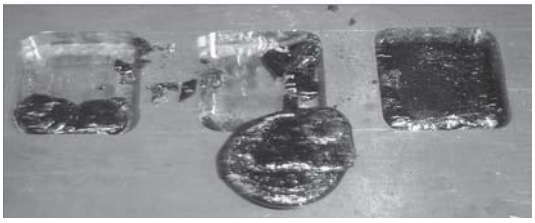

Figure 1. The as-quenched amorphous materials of $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+\delta}$ (x = 1, 2, and 3).

3.2. Phase identification

The XRD patterns of the as-quenched materials are show in Figure 2, indicate amorphous behavior. The main peaks of the Bi-2201 amorphous was corresponded the XRD patterns of JCPDS card No. 46-543. The crystal structure of the amorphous materials are the tetragonal structure, the lattice parameters of $a = b = 0.3854$ nm and $c = 2.4311$ nm, the volume of unit cell of 3.6117×10^{-22} cm^3, the theoretical density of 7.80313 gcm^{-3} and 80 of theoretical density percentage. On the other hand, the Bi-2212 and Bi-2223 amorphous materials are obtained broad peaks of XRD patterns like the amorphous materials very difficultly identification peak for calculation crystalline parameters. Therefore, we identified the main peak of XRD patterns by using the Powder Cell calculation. It found that, the lattice parameter $a = b = 0.38$ nm, $c = 3.0178$ nm and $a = b = 0.3879$ nm, $c = 3.8643$ nm, respectively. However, the main peak XRD patterns of Bi-2212 and Bi-2223 amorphous materials are high intensity at around, indicate the short-range atomic order (Aksan M.A. et al., 2004).

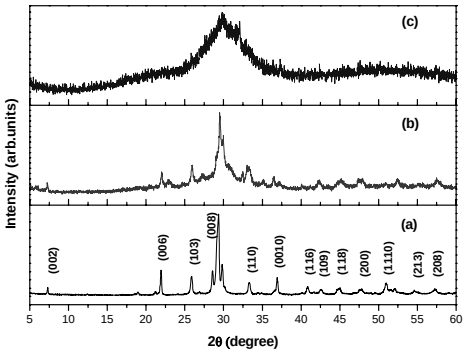

Figure 2. X-ray diffraction patterns of (a) Bi-2201, (b) Bi-2212, and (c) Bi-2223 amorphous materials.

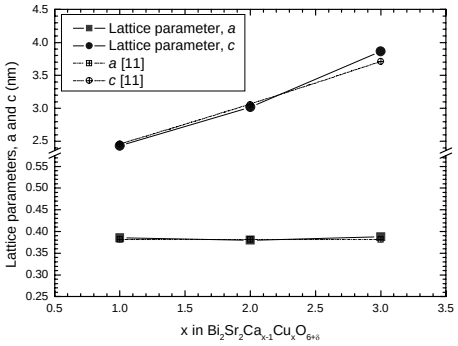

Figure 3. Variation of the lattice parameters a and c with different contents of Cu in $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+\delta}$ (x = 1, 2, and 3) samples and comparisons with the J.M. Tarascon et al. (Terascon J.M. et al., 1988).

The a, b and c lattice parameters of Bi-2201 amorphous is similarly, small slightly for Bi-2212 and Bi-2223 amorphous materials are comparison with a reported J.M. Terascon et al. (Terascon J.M. et al., 1988) as shown in Figure 4 because of lattice parameters of Bi-2212 and Bi-2223 amorphous materials are obtained data from only calculation.

3.3. Crystal structure

We have simulated the crystal structure of BSCCO system by using the VICS software as shown in Figure 3.

It found that, the Bi-2201 has a CuO_2 layer is sandwiched in between two BiO and SrO layers. The Bi-2212 has the $CaCuO_2$ layer inserted in between the SrO layers. The Bi-2223 has added $CaCuO_2$ layer, and three CuO_2 layers sandwiched in between the SrO layers.

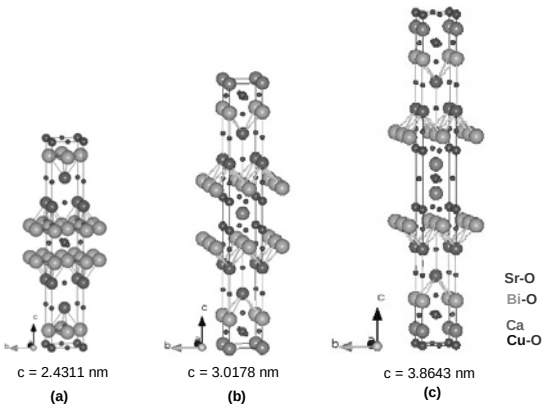

Figure 4. Crystallographic cells of (a) Bi-2201, (b) Bi-2212, and (c) Bi-2223

3.4. Microstructure

The powder amorphous materials are observed the microstructure by the SEM as shown in Figure 5, indicate the glass ceramics behavior.

The surface morphologies of Bi-2201, Bi-2212, and Bi-2223 amorphous materials are show in Figure 6 (a), (b), and (c), respectively.

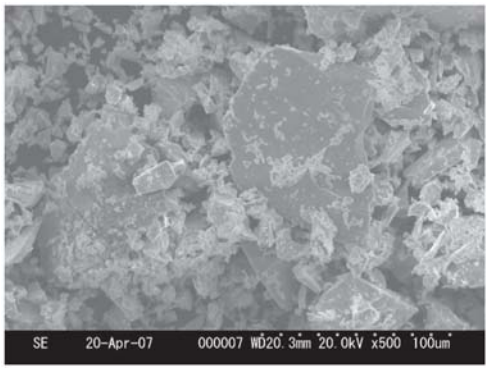

Figure 5. Morphologies of the powder amorphous materials

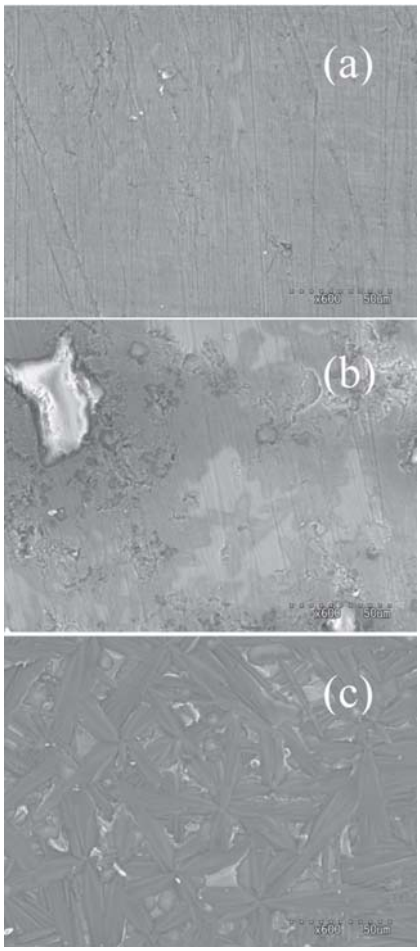

Figure 6. Scanning electron micrographs of surface (a) Bi-2212, (b) Bi-2212, and (c) B-2223 as quenched and polished the amorphous materials

3.5. Vickers hardness

The Vickers hardness of Bi-2201, Bi-2212, and B-2223 amorphous materials are determined according to the following formula:

$$H_V = \frac{1.844F}{l^2} \quad (1)$$

where F is the applied load in N, l is the average length of diagonal of an indentation in mm.

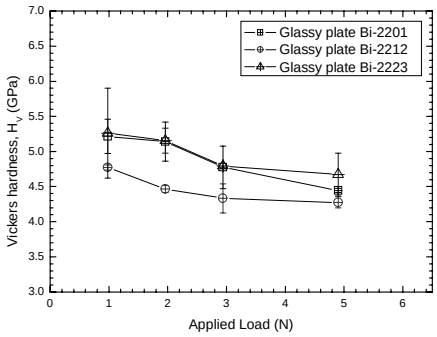

Figure 7. The relationship between the Vicker's hardness and applied load of Bi-2201, Bi-2212, and B-2223 amorphous materials

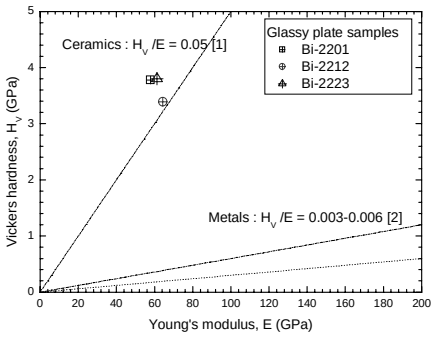

Figure 8. The relationship between the Vicker's hardness and Young's modulus of Bi-2201, Bi-2212, and B-2223 amorphous materials

It can be observed that at all the applied loads, there is a marked hardness increase such as at 0.49 N, from 4.3 to 4.7 GPa; this initial increase might be due to accounted for by the fact that the presence of large volume fraction of superconducting phases strengthen the connecting bridge between grains (Khalil S.M., 2007). The relationship between the Vickers hardness and Young's modulus of amorphous materials are shown in Figure 8.

The Bi-2201, Bi-2212, and Bi-2223 amorphous materials are related by the Young's modulus and the Vickers hardness given by:

$$E = 16.8067\, H_V \quad (2)$$

and the H_V / E values are nearly the ceramic properties.

In addition, we predicted the thermal conductivity (κ) by the following:

$$\kappa = \frac{3^{1/3}}{2^{1/6}\pi^{4/3}\gamma^2}\frac{k_B^3}{(2\pi)^3\hbar^3}Ma\Theta^2\frac{\Theta}{T} \quad (3)$$

where γ is the Grüneisen constant, k_B is Boltmann constant, M is the mass of a unit cell, $\hbar$ is constant, and a is annihilation operators of the dimension of displacement (Roufosses M. and Klemens P.G., 1973).

From the equation (3) is indicated that the κ depends directed to Debye temperature, following by:

$$\kappa \propto \Theta \quad (4)$$

It might be due to the predication of the of BSCCO amorphous materials are maybe $\kappa_{\text{Bi-2201}} < \kappa_{\text{Bi-2212}} < \kappa_{\text{Bi-2213}}$, we will measure it soon.

Table 1 Characteristic of Bi-2201, Bi-2212, and Bi-2223 amorphous materials

Density (gcm^{-3})	6.2730	5.8137	4.6422
Atomic weight (g)	$2.81823x10^{-21}$	$2.95138x10^{-21}$	$3.05769x10^{-21}$
Lattice parameter a (nm)	0.3854	-	-
Lattice parameter b (nm)	0.3854	-	-
Lattice parameter c (nm)	2.4311	-	-
Volume of unit cell (cm^3)	$3.6117x10^{-22}$	-	-
Theoretical density; TD (gcm^{-3})	7.80313	-	-
% of T.D	80	-	-
Longitudinal sound velocity; v_L (ms^{-1})	3327.2	3643.9	3981.1
Shear sound velocity; v_S (ms^{-1})	1920.9	2103.8	2298.5
Vickers hardness; H_V (GPa)	3.7821	3.3926	3.8022
Young's modulus; E (GPa)	57.8691	64.3278	61.3134
Bulk modulus; K (GPa)	38.58	42.89	40.88
Shear modulus; G (GPa)	23.15	25.73	24.53
Poision's ratio	0.25	0.25	0.25
Compressibility; β (10^3GPa)	25.92	23.32	24.46
Debye temperature; Θ (K)	270.72	284.99	306.00

4. Summary and conclusions

The initial composition of $Bi_2Sr_2Ca_{x-1}Cu_xO_{6+\delta}$ (x = 1, 2, and 3) melted at 1,200 ^oC for 30 min and quenched at room temperature to obtained the amorphous materials. It is due to the formation of the crystal structure, the glass ceramic, and the amorphous behavior as analyzed from XRD patterns, Powder Cell, VICS, and SEM studies. The BSCCO amorphous materials have been the H_V/E values correspond the ceramic properties.

Finally, the thermal conductivity of BSCCO amorphous materials are predicted by the Debye temperature. It might be the $\kappa_{\text{Bi-2201}} < \kappa_{\text{Bi-2212}} < \kappa_{\text{Bi-2213}}$, and corresponding to a good thermoelectricity

Acknowledgements

This work had financial support from Research and Development Institute, Sakon Nakhon Rajabhat University and computer support Science center Sakon Nakhon Rajabhat University Thailand. Division of Sustainable Energy and Environmental Engineering, Graduate School of Engineering, Osaka University, Japan for using apparatus measured mechanical properties.

References

Aksan M.A. and Yakinci M.E.2004.Synthesis and characterization of Er-substituted Bi-2223 H-T_c glass-ceramic superconductors. **Journal of Alloys Compounds** (385) 33-43.

Chatterjee S., Banerjee S., Mollah S. and Chaudhuri B.K.1996.Transport properties of Pb-doped $Bi_4Sr_3Ca_3Cu_4O_x$ semiconducting glasses and glass-ceramic superconductors. **Physical Review B** (53) 5942-5952.

Chatterjee S., Pal P.K., Bhattacharya S. and Chaudhuri B.K. 1998.Depression of superconductivity and the phonon-drag effect in glass-ceramic superconductors obtained by annealing the Fe-doped $(Bi, Pb)_4Sr_3Ca_3Cu_{4-m}Fe_mO_x$ glassy precursor. **Physical Review B** (58) 12427-12432.

Khalil S.M. 2007. Influence of alkaline metal Li1+ intercalation on the excess conductivity, thermopower and hardness of BSCCO pellets. **Physica B** (391) 130-135.

Maeda H., Tanaka Y., Fukutumi M. and Asano T.1988. A new high-T_c oxide superconductor without a rare earth element. **Japanese Journal of Applied Physics** (27) L209-210.

Roufosses M. and Klemens P.G.1973. Thermal conductivity of complex dielectric crystals. **Physical Review B** (7) 5379-5386.

Sales B.C.1998 Electron crystals and phonon glasses: a new path to improved thermoelectric materials. **Materials Research Society Bulletin** (23) 15-21.

Seetawan T.1998. Superconducting whiskers growth of $Bi_2Sr_2CA_2Cu_3O_{10}$. **M.S. thesis,** Chiang Mai University. Thailand.

Slack G.A.1995. **Thermoelectric Handbook** (ed. Rowe, M.) CRC. Boca Raton.

Som K.K. and Chaudhuri B.K.1990. Electrical and dielectric properties of the $Bi_4Sr_3Ca_3Cu_4O_x$ (4:3:3:4) glassy semiconductor. **Physical Review B** (41) 1581-1591.

Tarascon J.M., Mckinnon W.R., Barboux P., Hwang D.M., Bagley B.G., Greene L.H., Hull G.H., LePage Y., Stoffel N. and Giround M.1988. Preparation, Structure, and properties of the superconducting compound series $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ with n = 1, 2, and 3. **Physical Review B** (38): 8885-8892.