Effect of milling techniques on the particle characteristics of conductive Pr-substituted YBa$_2$Cu$_3$O$_{7-y}$ compound

P. Prayoonphokkharat$^{1,2,3}$, P. Wannasut$^4$, C. Sripachuabwong$^{4,8}$, A. Tuantranont$^{4,5}$ and A. Watcharapasorn$^{1,4,6,*}$

$^1$ Department of Physics and Materials Science, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

$^2$ Graduate School, Chiang Mai University, Chiang Mai 50200, Thailand

$^3$ Department of Science, Takpittayakhom School, Tak 63000, Thailand

$^4$ Center of Advanced Materials for Printed Electronics and Sensors, Materials Science Research Center, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand

$^5$ Thailand Organic and Printed Electronics Innovation Center, National Electronics and Computer Technology Center, National Science and Technology Development Agency, Klong Luang, Pathumthani 12120, Thailand

$^6$ Center of Excellence in Materials Science and Technology, Materials Science Research Center, Chiang Mai University, Chiang Mai 50200, Thailand

E-mail: anucha@stanfordalumni.org

Abstract. In this work, the effects of milling techniques on Pr-substituted YBa$_2$Cu$_3$O$_{7-y}$ (YPrBCO) particles were investigated. The Pr-substituted YBa$_2$Cu$_3$O$_{7-y}$ powders were prepared by solid-state reaction method. The stoichiometric mixtures of Y$_2$O$_3$, BaCO$_3$, CuO and Pr$_6$O$_{11}$ starting powders were calcined at 880 °C for 12 h in air to form respective compounds. The resulting products were milled for 4 – 12 h using the conventional ball milling technique and for 4 h using the high-energy planetary ball milling method. The phase and structure identification of powders were characterized by X-ray diffraction (XRD) technique. The microstructure and chemical composition were studied using scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS). The XRD patterns indicated that the pure phase of YPrBCO powders was obtained. For this material system, the conventional ball mill technique gave particles having a relatively wide particle size distribution with a maximum size of ~2 µm regardless of milling time. In contrast, the narrower particle size distribution was observed for the YPrBCO powder obtained from the high-speed ball milling method and the largest particle size did not exceed 100 nm. These results showed that the powder produced by the high-speed ball milling technique could have a potential use in colloidal solution for printed thermoelectric film.

1. Introduction

For large-scale thermoelectric device fabrication, several attractive techniques are solution-based printing processes such as inkjet printing and screen printing because of their simplicity, affordability, low cost, and eco-friendliness [1,2]. In screen printing, ink is deposited through a porous printing plate made from a mesh that is affixed to a rigid frame. For this system, the ink must flow under shear stress but quickly set up elastically upon relaxation [1]. Therefore, the highly homogeneous composition as
well as with desirable size of less than 1 μm and narrow particle size distribution of powder precursor are important factors for a suitable printing solution [3].

Recently, metal-oxide nanoparticles have been the subject of much interest because of their properties which differ from the bulk. Reducing the particle size and controlling the morphology often results in the dramatic changes in properties during the direct incorporation into device via microfabrication process [4,5]. For thin film thermoelectric (TE) devices, their nanostructures showed not only smaller size but also improved ZT value due to an increase in Seebeck coefficient by quantum size effect and a decrease in thermal conductivity from enhanced phonon scattering [6,7].

High-\textit{Tc} \text{YBa}_2\text{Cu}_3\text{O}_{7-y} (\text{YBCO}) cuprate oxide superconducting compound is one of the best materials for superconductor applications including magnets, power transmission line and generators [4,8,9]. It has an orthorhombic perovskite structure for superconducting phase (123-phase) [10]. Its superconducting properties may be affected by defects induced in the structure. With the presence of oxygen vacancies, the YBCO ceramics with rather good thermoelectric properties have been obtained as reported by Prayoonphokkharat et al [11] and Wannasut et al [12]. Another way to manipulate the electrical properties of YBCO is through the Y-site substitution by ions such as Sn, Ce, Sm, Dy, Zn previously investigated by many researchers [9, 13-17]. One 123-type compound of our interest is \text{PrBa}_2\text{Cu}_3\text{O}_{7-y} (\text{PrBCO}) which has a structure isomorphic to YBCO but its electronic structure and charged carrier transport behavior causes this compound to be a semiconductor [18,19]. The substitution of Pr into YBCO is therefore expected to dramatically change the electrical conductive behavior in this 123-type compound.

A variety of preparation methods such as chemical solution, sol-gel, metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition (PLD), citrate-pyrolysis and solid-state reaction have been used to synthesize \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y} (\text{YPrBCO}) [20-23]. Despite being the simplest method with industrial-scaled synthesis capability, the solid state reaction requires a careful control of the composition of starting reactants and calcination procedures which, in turn, play significant roles in phase formation and the characteristic of synthesized nanoparticles [4,10]. For example, by substitution of Pr for Y, the \text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-y} solid solution having particle size in a range of 1-20 μm (and 50 – 100 μm agglomerates) was obtained along with \text{BaCuO}_2 and \text{CuO} second phases [18, 24-27]. In terms of size and phase requirements, these particles were not yet suitable for being used in ink jet or screen print solution.

Therefore, this research attempts to synthesize pure Pr-substituted \text{YBa}_2\text{Cu}_3\text{O}_{7-y} powders by the solid-state reaction method. Post grinding and milling procedures are employed to reduce the particle size. The relationships between phase, structure and chemical composition of these powders are established and discussed in detail.

2. Experimental
The Pr-substituted \text{YBa}_2\text{Cu}_3\text{O}_{7-y} (\text{Y}_{0.5}\text{Pr}_{0.5}\text{Ba}_2\text{Cu}_3\text{O}_{7-y} or \text{YPrBCO}) powder was fabricated by solid-state reaction method. The starting powders of \text{Y}_2\text{O}_3, \text{BaCO}_3, \text{CuO} and \text{Pr}_6\text{O}_{11} were mixed in a desired stoichiometric ratio by wet-ball milling method for 24 h in ethanol. The mixture was dried and calcined in an open alumina crucible at 880 °C for 12 h in the normal air atmosphere. The resulting \text{YPrBCO} powder was divided into 5 parts. The first part was manually ground in an agate mortar (i.e. unmilled sample). The second to the fourth parts were milled via conventional ball milling technique for 4, 8 and 12 h, respectively. The last part was milled for 4 h using the high-energy planetary ball milling instrument with a milling speed of 1000 rpm. The ball-to-powder ratio of all milling techniques was about 8:1. The powders were characterized for phase identification by X-ray diffraction (Rikagu Smartlab) with CuKa ($\lambda = 1.5405$ Å) radiation over 20 angle range of 10 – 60°. The microstructural analysis was carried out using scanning electron microscopy (JEOL-JT300) and the elemental composition were deduced by energy dispersive X-ray analysis (SEM-EDS).
3. Results and Discussion
The XRD patterns of the unmilled, conventional ball milled and high-speed ball milled samples are shown in Figure 1. For the unmilled and conventional ball milled samples, pure phase of YPrBCO was obtained and X-ray peaks corresponded to the standard data of JCPDS file No. 01-079-0312, indicating an orthorhombic structure [18,19,25]. The quantitative analysis on the XRD patterns of YPrBCO powders was carried out by the Rietveld refinement procedure using MAUD program [28]. It was found that a small amount (< 1-2 wt%) of BaCuO$_2$ secondary phase was present in all samples. BaCuO$_2$ could form from BaCO$_3$ and CuO via the following reaction [13]:

$$\text{BaCO}_3 + \text{CuO} \rightarrow \text{BaCuO}_2 + \text{CO}_2$$  \hspace{1cm} (1)

Except for the unmilled sample, the presence of BaCO$_3$ in the milled powder could originate from the degradation of the powder due to localized heating by mechanical force (despite the fact that the cooling system was used during milling) in which the residual Ba could react with CO$_2$ as previously observed in the fabrication of YBCO nanoparticles [4, 29-31]. The amount of BaCO$_3$ in this study was found to be < 1 wt% for the conventional ball milled sample and ~7 wt% in the high speed ball milled sample. Nevertheless, this phase was found to disappear after post heat treatment (or sintering) in oxygen atmosphere [29].

In addition, from the XRD data, the crystallite size of all samples was estimated using the Scherrer equation [32],

$$D = \frac{K\lambda}{\beta \cos \theta}$$  \hspace{1cm} (2)

where $K$ is the Scherrer’s constant, $\lambda$ the X-ray wavelength, $\beta$ the full width at half maximum (FWHM) and $\theta$ the XRD peak position (i.e. one half of 2$\theta$). The estimated crystallite size values of YPrBCO powders are shown in Table 1. It was found that for the unmilled sample, the crystallite size was about 28.3 nm. For the conventional ball milled powders, the crystallite size of YPrBCO powders decreased from 27.7 to 20.9 nm when the milling time increased from 4 to 12 h, respectively. For the high speed ball milled sample, the broadening of the XRD peaks (compared to those of the conventional ball milled samples) gave the smallest crystallite size of about 15.9 nm despite the fact that the milling time used was only 4 h. The microstrain in the crystallites may also play a role in the peak broadening. Although the estimated crystallite size of all samples was in nanometer range, the actual particle size was much larger as observed in the SEM images described in the next section.
Figure 1. XRD patterns of unmilled, conventional ball milled and high speed ball milled YPrBCO samples.

Table 1. Estimated crystallite size and particle size range of YPrBCO powders for different milling conditions.

| Condition                        | Crystallite size (nm) | Particle size range (µm) |
|----------------------------------|-----------------------|--------------------------|
| Unmilled                         | 28.3                  | 1 – 5                    |
| Conventional ball milled for 4 h | 27.7                  | 1 – 2                    |
| Conventional ball milled for 8 h | 21.8                  | 0.2 – 2                  |
| Conventional ball milled for 12 h| 20.9                  | 0.1 – 2                  |
| High speed ball milled for 4 h   | 15.9                  | 0.05 – 0.1               |

Figure 2 shows the SEM micrographs of the unmilled (Figure 2(a)), conventional ball milled (Figure 2(b)-(d)) and high speed ball milled (Figure 2(e)) YPrBCO samples. The microstructure of the powders exhibited an irregular shape. The particle size of the unmilled sample was in a range of 1-5 µm whereas the milled samples showed smaller particle sizes. For example, using the conventional ball milling for 4 h could reduce the particle size to 1-2 µm and longer milling time further decreased the particle size as shown in Table 1. A closer look at high magnification revealed that the particles appeared as a clump of fine crystals of about 200 – 300 nm size for 8 h-milled sample (Figure 2(c)) and 100-200 nm for 12 h-milled sample (Figure 2(d)). For the high speed ball milling sample (Figure 2(e)), the particles had more spherical shape with particle size in a range of 50-100 nm. Thus, these results confirmed that the high speed ball milling for 4 h could effectively produce nanoparticles compared to the conventional ball milling method. In terms of size, size distribution and shape of the prepared particles, it seems that the high speed ball milled powder was most suitable to be incorporated into a printing solution with a suitable solvent [6]. It has previously been shown that the printed thermoelectric thin film of some non-oxide compounds showed good thermoelectric behavior due to the nanostructuring and low-dimensional effects [6,7,33,34]. Therefore, the solution formulation and the suitable post heat treatment steps of this oxide compound will be further investigated for the optimum printing process.
Figure 2. Microstructure of YPrBCO powders: (a) unmilled, (b) conventional ball milled for 4 h, (c) 8 h, (d) 12 h and (e) high speed ball milled for 4 h.

Table 2 shows the elemental analysis using energy dispersive X-ray analysis (EDS). It was found that the approximate nominal composition of (Y+Pr) : Ba : Cu of samples was closed to 1 : 2 : 3. However, for the high speed ball milled samples, the reliable elemental composition could not be obtained due to the rather small particle size compared to the resolution (~1-2 µm) of the SEM-EDS system. However, the composition of the main phase in this sample should be comparable to the other samples based on their similar XRD patterns.
Table 2. Estimated elemental composition of YPrBCO samples for different milling conditions.

| Condition                     | Elemental composition (%at.) |
|-------------------------------|-----------------------------|
|                               | Y  | Pr | Ba | Cu | O  |
| Unmilled                      | 3.86 | 3.98 | 11.09 | 26.64 | 54.43 |
| Conventional ball milled for 4 h | 4.99 | 4.38 | 14.03 | 29.41 | 47.18 |
| Conventional ball milled for 8 h | 4.06 | 4.72 | 12.32 | 25.82 | 53.08 |
| Conventional ball milled for 12 h | 4.56 | 4.75 | 11.38 | 24.86 | 54.44 |
| High speed ball milled for 4 h | N/A          |

* N/A – The elemental composition could not be determined due to the limitation of the EDS technique.

4. Conclusions
This research showed the effect of milling techniques on particle characteristics of conductive Pr-substituted YBa$_2$Cu$_3$O$_{7-y}$ compound prepared by solid state reaction under normal air atmosphere. X-ray diffraction analysis indicated pure YPrBCO powders with an orthorhombic structure. The crystallite size and microstrain caused the broadening of the XRD peaks in high speed ball milled sample. The microstructure showed a rather large particle size in micrometer range with wide particle size distribution for the conventional ball milled sample compared to the nanoparticles observed in the high speed ball milled sample. The result of chemical composition measurement by EDS showed that the (Y+Pr):Ba:Cu was closed to 1:2:3. Thus, these results suggested that the high speed ball milling method could effectively produce the nanoparticle powders suitable for the fabrication of printed thermoelectric film.

Acknowledgements
This research was financially supported by the Thailand Research Fund and TA/RA (2560-2561) scholarships, Graduate School, Chiang Mai University. Partial supports from the Center of Advanced Materials for Printed Electronics and Sensors (CMU-NECTEC), Center of Excellence in Materials Science and Technology, Faculty of Science, the Graduate School, Chiang Mai University, and Takpittayakhom School are also acknowledged. Authors would also like to thank Thailand Organic and Printed Electronics Innovation Center (TOPIC), National Electronics and Computer Technology Center (NECTEC), National Science and Technology Development Agency (NSTDA), A. Tuantranont gratefully acknowledges the Thailand Research Fund for TRF Research Team Promotion Grant (RTA6180004). P. Prayoonphokhharat would also like to thank the financial support from the TRF through the Royal Golden Jubilee Ph.D. Program (PhD 0106/2560).

References
[1] Orrill M, LeBlanc S 2016 Printed thermoelectric materials and devices: Fabrication techniques, advantages, and challenges J. Appl. Polym. Sci. 134(3)
[2] Park S, Lee D 2016 Effects of the particle size and the solvent in printing Inks on the capacitance of printed parallel-plate capacitors Electronics 5(1) 7
[3] Przybylski K, Brylewski T, Bućko M, Prażuch J, Morawski A, Łada T 2003 Synthesis and properties of superconducting (Hg,Re)–Ba–Ca–Cu–O thick films on polycrystalline LaAlO$_3$ substrate obtained by screen-printing method Physica C 387(1), 225-229
[4] Alikhanzadeh-Arani S, Salavati-Niasari M, Almasi-Kashi M 2013 Influence of the utilized precursors on the morphology and properties of YBa$_2$Cu$_3$O$_{7-y}$ superconducting nanostructures Physica C 488, 30-34
[5] Nasui M, Mos R.B, Gabor M.S, Petrisor T, Tomolea A, Ware E, Goga F, Mesaros A, Ciontea L 2017 New versatile synthesis for low dimension superparamagnetic YBa$_2$Cu$_3$O$_{7-x}$ nanoparticles Ceram. Int. 43(12), 8845-8849
[6] Lu Z, Layani M, Zhao X, Tan L.P, Sun T, Fan S, Yan Q, Magdassi S, Hng H.H 2014 Fabrication of flexible thermoelectric thin film devices by inkjet printing small. 10(17), 3551-3554
[7] Ou C, Sangle A.L, Chaliklen T, Jing Q, Narayan V, Kar-Narayan S 2018 Enhanced thermoelectric properties of flexible aerosol-jet printed carbon nanotube-based nanocomposites Apl. Mater. 6(9), 096101

[8] Prayoonphokkharat P, Jiansirisomboon S, Watcharapasorn A 2013 Fabrication and properties of YBa2Cu3O7-x ceramics at different sintering temperatures Electron. Mater. Lett. 9(4), 413-416

[9] Zhang L, Sun X.F, Chen X, Zhang H 2003 Different effects of Zn and Pr doping on YBa2Cu3O7-y Physica C 386, 271-274

[10] Rodriguez J.E, Lopez J 2007 Thermoelectric figure of merit of oxygen-deficient YBCO perovskites Physica B 387(1), 143-146

[11] Prayoonphokkharat P, Watcharapasorn A 2017 Transport properties and thermoelectric figure of merit of YBa2Cu3O7-xBa0.5Na0.5TiO3 ceramics Sci. Adv. Mater. 9(10), 1872-1875

[12] Wannasut P, Prayoonphokkharat P, Jaiban P, Keawprak N, Watcharapasorn A 2019 Thermoelectric properties of YBa2Cu3O7-xNa0.5Co0.5 segmented oxide ceramics Mater. Lett. 236, 378-382

[13] Andreouli C, Tsetsekou A 1997 Synthesis of HTSC Re(Y)Ba2Cu3Ox powders: the role of ionic radius Physica C 291(3), 274-286

[14] Hari Babu N, Iida K, Shi Y, Cardwell D.A 2008 Processing of bulk Sm–Ba–Cu–O nano-composite superconductors Physica C 468(15), 1340-1344

[15] Lei S, Yunsong H, Wenhua P, Xianming L, Liangbin W, Xiao-Guang L, Guien Z, Yuheng Z 1997 Study on the Pr-doped and Ce-doped YBa2Cu3O7 system by XPS and Raman spectrum Physica C 282-287, 1021-1022

[16] Zhang D.Y, Wang G.M, Wang Y.X, Wang Z, Zhang Y.H 1990 Influence of high Sn concentrations on the structure and properties of Y-Ba-Cu-O compounds Solid. State Commun. 75(8), 629-632

[17] Zhang H, Zou X.W, Wang Z.H, Chen Y.X 2000 A comparative investigation of oxygen indiffusion in the orthorhombic phase of REBCO (RE: Y, Sm, Nd) by in situ electrical resistance Physica C 337(1), 307-311

[18] Kyoichi K, Azusa M, Hiroyuki S, Takao I, Takao W, Tomoaki Y 1988 Crystal Structure and Superconductivity in Ba2Y1-Pr3Cu3O7-δ Jpn. Appl. Phys. 27(9A), L1642

[19] Singhal R.K 2011 A comparative study of Pr substitution at Y and Ba sites in YBa2Cu3O7-δ Mater. Lett. 65(5), 825-827

[20] Barnes P.N, Murray P.T, Haugan T, Rogow R, Perram G.P 2002 In situ creation of nanoparticles from YBCO by pulsed laser deposition Physica C 377(4), 578-584

[21] Huhtinen H, Laiho R, Lähderanta E, Paturi P, Raatila J, Stepantov Y 2000 YBCO nanopowder: novel material for PLD preparation of thin films Physica C 341-348, 2377-2378

[22] Jasim S.E, Jusoh M.A, Hafiz M, Jose R 2016 Fabrication of superconducting YBCO nanoparticles by electrospinning Procedia. Engineer. 148, 243-248

[23] Xu X.L, Guo J.D, Wang Y.Z, Sozzi A 2002 Synthesis of nanoscale superconducting YBCO by a novel technique Physica C 371(2), 129-132

[24] Matsuda A, Kinoshita K, Ishii T, Shibata H, Watanabe T, Yamada T 1988 Electronic properties of Ba2Y1-xPrxCu3O7-δ Phys. Rev. B. 38, 2910(R)

[25] Bin O, Michikazu K, Hiroshi N, Koh T, Masatsune O 1988 Preparation and physical properties of (Pr1-x)Y1-xBa2Cu3O7 Jpn. Appl. Phys. 27(1A), L41

[26] Kamat R.V, Vittal Rao T.V, Pillai K.T, Vaidya V.N, Sood D.D 1991 Preparation of high grade YBCO powders and pellets through the glycerol route Physica C 181(4), 245-251

[27] Wannasut P, Keawprak N, Jaiban P, Watcharapasorn A 2018 Preparation and physical properties of segmented thermoelectric YBa2Cu3O7-xCa3Co4O9 ceramics Iop. Conf. Ser. Mat-Sci. Eng. 303(1), 012010
[28] Lutterotti L, Matthies S, Wenk HR 1999 MAUD: a friendly java program for material analysis using diffraction IUCr: Newsletter of the CPD 21, 14-15

[29] Baszynski J 1993 Mechanochemical effects of griding on the YBa$_2$Cu$_3$O$_{7-x}$ superconductor J. Alloy. Compd. 195, 683-686

[30] Martirosyan K.S, Galstyan E, Xue Y.Y, Luss D 2008 The fabrication of YBCO superconductor polycrystalline powder by CCSO. Supercond. Sci. Tech. 21(6), 065008

[31] Shen Z, Hu Y, Fei L, Li K, Chen W, Gu H, Wang, Y 2015 Photocatalytically active YBa$_2$Cu$_3$O$_{7-x}$ nanoparticles synthesized via a soft chemical route J. Nanomater. 2015, 5

[32] Alexander L, Klug H.P 1950 Determination of crystallite size with the X-ray spectrometer J. Appl. Phys. 21(2), 137-142

[33] Lee H.B, We J.H, Yang H.J, Kim K, Choi K.C, Cho BJ 2011 Thermoelectric properties of screen-printed ZnSb film. Thin Solid Films 519(16), 5441-5443

[34] Ou C, Sangle A.L, Datta A, Jing Q, Busolo T, Chalklen T, Narayan V, Kar-Narayan S 2018 Fully printed organic–inorganic nanocomposites for flexible thermoelectric applications Acs. Appl. Mater. Inter. 10(23), 19580-19587