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ANALYSIS OF THERMOGRAVIMETRIC (TG) AND INFRA-RED (FTIR) ON Dy SUBSTITUTION IN Bi(Pb)-2223 SUPERCONDUCTOR

(Analisis Termogravimetri (TG) dan Infra-Merah (FTIR) ke atas pemasukan Dy dalam Superkonduktor Bi(Pb)-2223)

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Abstract

In this paper, the results of the thermal and infra-red analysis of Dy substituted in Bi (Pb)-2223 superconductor have been studied by thermogravimetric (TG) and Fourier transform infrared (FTIR). The samples with nominal composition of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ where x = 0.000, 0.025, 0.050, 0.100, and 0.200 were prepared by co-precipitation (COP) method using metal acetate as the starting salts. The mechanism of thermal analysis of the precursor powder for each stage (drying, precalcine, and calcine) were studied from 20 °C to 920 °C by 5 °C/min of heating rate. Interestingly, the thermal decomposition proceeds in the almost similar way regardless of the Dy substitution level with five major drops at the drying stage. Based on TG curves results, the temperature range from 840 °C to 850 °C can be suggested as an optimum calcination and sintering temperature. The majority of decomposition step which related to the loss of water from oxalate was in the range of 100 °C to 200 °C while the formation of precipitation into Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, and Dy_2O_3 were in the range of 210 °C to 360 °C. From the FTIR result, all the precursor powders qualitatively showed four main regions and the existence of –OH group can increase the diffusion rate between metals during the synthesis process.

Keywords: dy-substitution, BSCCO, superconductor, FTIR, thermogravimetric analysis

Abstrak

Dalam laporan ini, keputusan analisa terma dan infra-merah terhadap pemasukan Dy di dalam superkonduktor Bi (Pb)-2223 telah dikaji melalui termogravimetri dan transformasi fourier infra-merah (FTIR). Semua sampel dengan komposisi nominal $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ dimana x = 0.000, 0.025, 0.050, 0.100 dan 0.200 telah disediakan melalui kaedah ko-pemendakan (COP) dengan menggunakan logam asetat sebagai garam pemula. Mekanisma analis terma terhadap serbuk pelopor untuk setiap peringkat (pengeringan, pra-pengkalsinan dan pengkalsinan) telah dikaji dari suhu 20 °C hingga 920 °C dengan kadar pemanasan 5°C/min. Menariknya, penguraian terma berlaku agak sama tanpa menghiraukan aras pemasukan Dy iaitu dengan lima jatuhan pada peringkat pengeringan. Berdasarkan kepada keputusan keluk TG, dicadangkan bahawa julat suhu dari 840 °C hingga 850 °C merupakan suhu pengkalsinan dan suhu sinteran optimum. Majoriti langkah penguraian yang berhubungkait dengan kehilangan air dari oksalat, berlaku dalam julat 210 °C hingga 360 °C manakala pembentukan pemendakan dalam Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, dan Dy_2O_3 adalah dalam julat 210 °C hingga 360 °C. Dari keputusan FTIR, semua serbuk pelopor secara kualitatifnya menunjukkan empat daerah utama dan keujudan kumpulan –OH boleh meningkatkan kadar peresapan antara logam semasa proses sintesis.

Kata kunci: pemasukan Dy, BSCCO, superkonduktor, FTIR, analisis termogravimetri

Introduction

Bi-2223 superconductor is one of the Bi-Sr-Ca-Cu-O systems that is reported to be difficult to synthesize as a single phase. Generally, solid-state reaction (SSR) method was used to prepare this superconductor material. However, several disadvantages are observed with this technique, such as high impurity content, inhomogeneity, large particle size and shape, and the requirement of a high temperature range with long calcination and sintering time. Therefore, several wet chemical methods including the co-precipitation (COP) method, have been developed to overcome these problems [1]. Powder that is produced by COP is better in chemical mixing since all cation species mixed in an atomic scale. Previously, the substitution of various elements in Bi-2223 is proven to be important to study due to the considerable change such as in superconducting, structural, mechanical, and transport properties. The thermal decomposition of COP samples gave valuable information of the precursors and also the optimum condition for SSR to obtain superconducting samples. Moreover, FTIR spectra could also be used to analyse the decomposition process of the precursor powder with different stages of the process. In this paper, we have reported the influence of Dy substitution on the TG and FTIR Analysis of Bi (Pb)-2223 superconductor prepared via co-precipitation method.

Materials and Methods

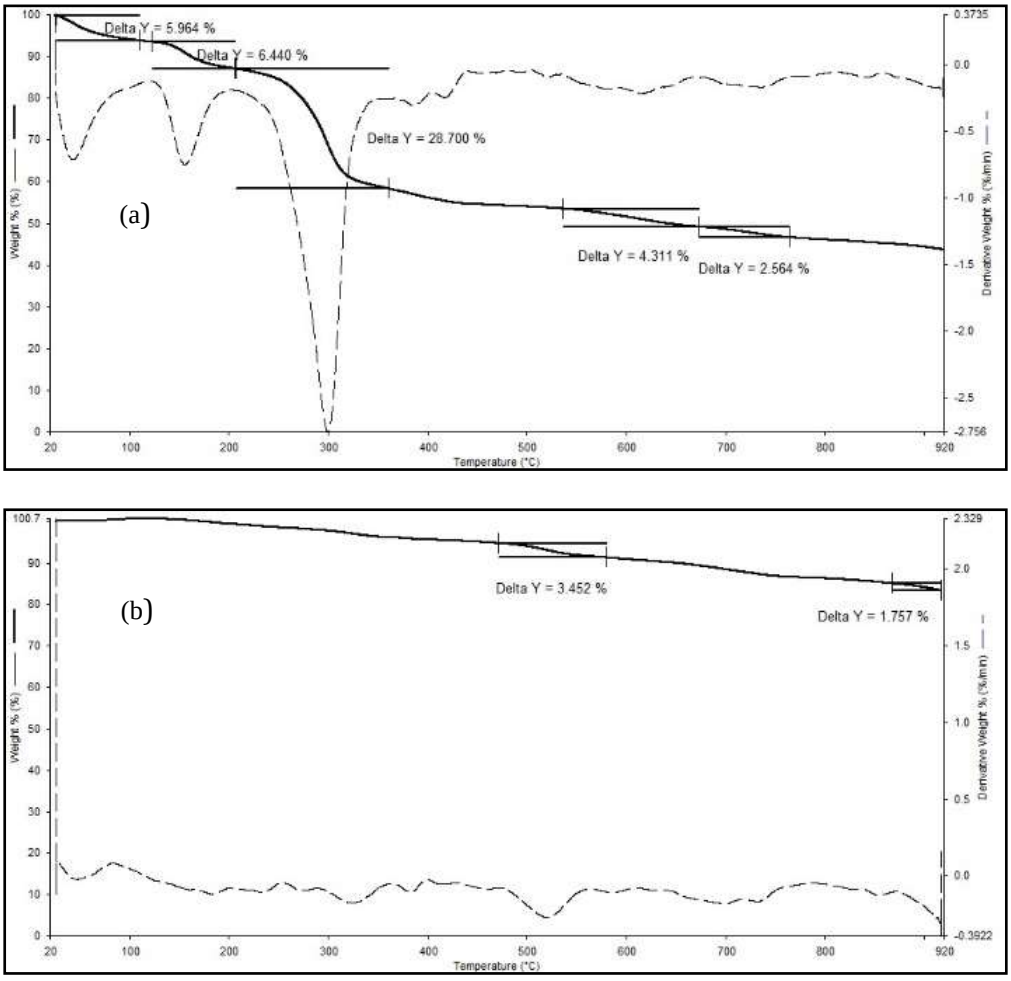
Sample of $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ (x = 0.000, 0.025, 0.050, 0.100, and 0.200) were prepared using co-precipitation (COP) method described in our previous paper [2]. The precipitated (drying at 60 °C), precalcine (750 °C for 12 hours) and calcine (845°C for 24 hours) powders were studied by TGA and FTIR instrument. In this study, TGA (Pyris 1) was used to analyze the mass change of the samples as a function of temperature. The powder was run by 5°C/min from 20 °C to 920 °C. The FTIR spectroscopy was used to investigate the mechanism of the COP transition. The IR absorption spectra of samples' powder were measured in the range of 400 cm^{-1} to 4000 cm^{-1} with a resolution of 4 cm^{-1} and recorded at room temperature using Spectrum 400 FT-1R/FT-NIR Spectrometer, Perkin Elmer.

Results and Discussion

The thermal analyses of the $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ precursor powder for each stage (drying, precalcine, and calcine) were studied from 20°C to 920°C by 5 °C/min of heating rate. Interestingly, the thermal decomposition proceeds in almost similar way regardless of the Dy substitution level. Figure 1 shows the TG curve for x = 0.025 Dy substituted sample.

The TG curves for x = 0.025 Dy substituted sample right after co-precipitation is displayed in Figure 1(a). According to the Figure 1(a), obviously there are five major drops. The weight loss occurred below 110 °C (5.964 %) was due to the evaporation of water and moisture loss from the powders. Similar behaviour has been reported for the evaporation of water and solvent molecules [3]. The second decomposition step in the range 120°C to 210°C (6.440 %) can be attributed to the loss of water molecule from $Bi_2(C_2O_4)_3$, $Pb(C_2O_4)$, $Sr(C_2O_4)$, $Ca(C_2O_4)$, $Cu(C_2O_4)$, and $Dy(C_2O_4)$ in which dehydrated oxalate were formed. This behaviour is confirmed by previous works [4]. In the range of 210°C to 360°C (28.700 %), weight loss were apparent in the decomposition of $Bi_2(C_2O_4)_3$ to Bi_2O_3, $Pb(C_2O_4)$ to PbO, $Sr(C_2O_4)$ to $SrCO_3$, $Ca(C_2O_4)$ to $CaCO_3$, $Cu(C_2O_4)$ to CuO, and $Dy(C_2O_4)$ to Dy_2O_3. Similar results shown by other researchers resulted in thermal decomposition of individual oxalates of Bi, Sr, Ca, and Cu [5]. Somehow, the decomposition of rare earth acetate took place at similar results which were around 200°C to 300°C [4, 5]. The next drop in the range of 540°C to 670°C (4.311 %) was the decomposition of $CaCO_3$ to CaO and in the range of 670°C to 760°C (2.564 %) was the decomposition of $SrCO_3$ to SrO. These results also had been proved by Popa et al. in which the decomposition of $CaCO_3$ to CaO took place in the range of 550 °C to 1000 °C and the decomposition of $SrCO_3$ to SrO took place in the range 600 °C to 1000 °C [5]. From the result, the weight of a stable metal oxide powder was obtained with 43.69 % of the sample weight.

The TG curves for the sample right after precalcine for 12 hours at 730°C and calcined for 24 hours at 845°C are shown in Figure 1(b) and (c) respectively. Based on Figure 1(b), the TG curves for x = 0.025 Dy substituted samples right after precalcine, obviously shows two major drops. As seen in the figure, the decomposition steps in the range 460°C to 770°C (3.452 %) and 850°C to 920°C (1.757 %) can be attributed to the decomposition of carbonate phase. This observation was in agreement with the results studied by previous works [6, 7]. These TGA result is in agreement with FTIR result and will be discussed later. From the Figure 1(c), the Dy substituted sample right after calcine for 24 hours at 845 °C, obviously shows one drop in the temperature above 820°C (3.044 %). Apparently, no indication of mass loss could be seen below 800°C for x = 0.025 Dy substituted in $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$. Therefore, it was revealed that the formation of the carbonate can be suppressed in the calcined stage. This result is slightly similar to other reports [7]. This observation will be supported by the result of FTIR later.



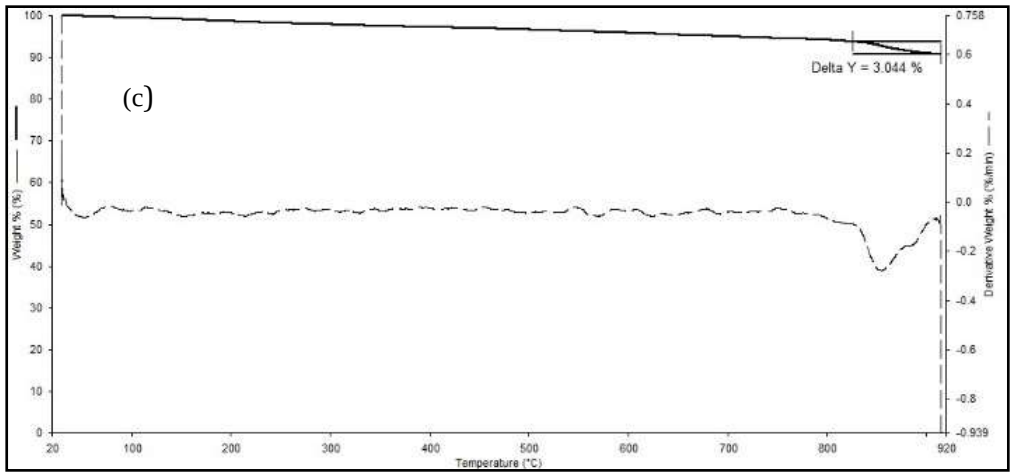


Figure 1. TGA of x = 0.025 Dy for (a) drying (b) precalcined (c) calcined stages

FTIR absorption spectra of a representative sample of Dy^{3+} substituted in $Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ where x = 0.025 superconductors recorded in the range between 400 cm^{-1} to 4000 cm^{-1} at room temperature are shown in Figure 2 and Table 1.

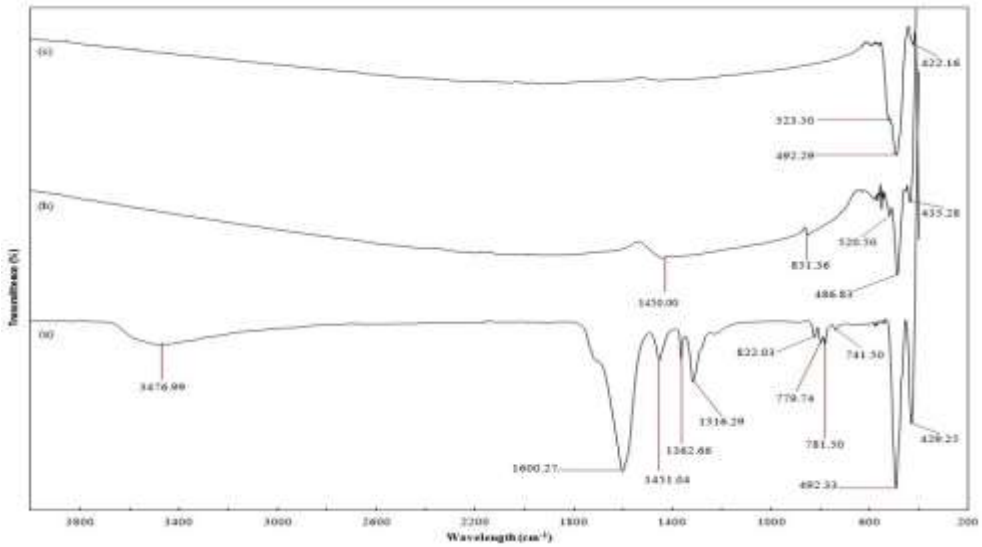


Figure 2. FTIR spectra of x = 0.025 Dy for (a) drying (b) precalcined (c) calcined stages

Table 1. The absorption bands in the FTIR Spectra right after co-precipitation, Precalcine, and Calcine for $x = 0.025$

Co-precipitation		Precalcine		Calcine	
Wavelength (cm^{-1})	**Assignment (ions)**	**Wavelength (cm^{-1})**	**Assignment (ions)**	**Wavelength (cm^{-1})**	**Assignment (ions)**
3476.99	O-H				
1600.27	-COO-				
1451.04	CO_3^{2-}	1450.00	CO_3^{2-}		
1362.66	C-C / C-O				
1316.29	C-C / C-O				
822.03	$SrCO_3$	851.36	$SrCO_3$		
779.74	M-O				
781.50	M-O				
741.50	M-O				
		520.55	M-O	523.50	M-O
492.33	M-O	486.83	M-O	492.29	M-O
429.25	M-O	435.28	M-O	422.16	M-O

Figure 2(a) shows the FTIR spectrum. The presence of broad absorption peaks in the range of 3700 cm^{-1} to 2900 cm^{-1} and a specific peak at about 3476.99 cm^{-1} correspond to the stretching vibration of intermolecular hydrogen band (O-H). The assignment of fundamental stretching of the OH groups is in agreement with previous reports [7]. The characteristic of absorption band due to carboxylate ion [-COO-] is presented around 1600.27 cm^{-1} which was confirmed as the complex formation in the BPSCCO system. The same observation of the presence of carboxylate ion was showed by other studies [8]. The presence of CO_3^{2-} is proven by the main peak absorption at approximately 1451.04 cm^{-1}, whereby this result is supported by Arshad et al. [7]. The characteristic bands of the oxalate group are evident at about 1362.66 cm^{-1} and 1316.29 cm^{-1} and are attributed to the stretching vibration of C-O and C-C. These observations are in agreement with earlier studies [8]. The peak at around 822.03 cm^{-1} is the characteristic for $SrCO_3$. Similar absorption band of $SrCO_3$ was observed in previous studied [7]. In addition, in the 800 cm^{-1} to 400 cm^{-1} region of the FTIR spectrum may be attributed to the characteristic of metal oxide (M-O) vibration. Similar behaviour had been reported for the M-O vibration [5, 7].

FTIR spectra for sample right after precalcine for 12 hours is shown in Figure 2(b). According to the result presented by precalcine at 750°C, the remaining volatile was removed and thus, changed the oxalates co-precipitation to a mixture of crystallized oxides and carbonates. The peaks for the carboxylate ion [-COO-] had disappeared in precursor precalcined. The presence of CO_3^{2-} carbonate group still remained and was proven by the main peak absorption at about 1450 cm^{-1}. The characteristic bands for the oxalate group had disappeared because the oxalate group were decomposed completely during the heat treatment 750°C for 12 hours supported by TGA results discussed earlier. Similar result was observed [7]. The characteristic for $SrCO_3$ at around 851.36 cm^{-1} still remained in this precalcine stage. The 800 cm^{-1} to 400 cm^{-1} region of the FTIR spectrum may be attributed to the characteristic of O-M vibration.

FTIR spectra for sample right after calcined for 24 hours at 845°C is shown in Figure 2(c). The presence of a CO_3^{2-} carbonate group and the peak for the characteristic of $SrCO_3$ had disappeared at calcine stage. This result is in agreement with previous studies [7]. This observation also had been supported by the TGA result discussed earlier,

whereby it was revealed that the formation of the carbonate can be suppressed in the calcine stage. The observed specific peaks at around 523.50, 492.29, and 422.16 cm^{-1} may be attributed to the characteristic of O-M vibration which is in agreement with the literature.

Conclusion

$Bi_{1.6}Pb_{0.4}Sr_2Ca_{2-x}Dy_xCu_3O_y$ superconducting samples prepared by COP method were investigated. From the TG curves of drying stages, the majority of the decomposition steps were the formation of precipitation into Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$, CuO, and Dy_2O_3 in the range of 200°C to 365°C. On the other hand, the decomposition of $SrCO_3$ to SrO and $CaCO_3$ to CaO took place in the range of 540 °C to 670 °C and 670 °C to 760 °C. According to the TG curves for the Dy substituted samples right after precalcine obviously showed two drops occurred. Apparently, no indication of mass loss could be seen below 800°C in the calcined stage. Therefore, it was revealed that the formation of the carbonate can be suppressed in this stage. FTIR results for Dy substituted precursor showed that the apparent FTIR was in the 800 cm^{-1} to 400 cm^{-1} region of the FTIR spectrum. The observation may be attributed to the characteristics M-O vibration.

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