UNIVERSITI PUTRA MALAYSIA

SYNTHESIS OF Er1-xAxBa2Cu3O7-δ (A=Ca, Zn, Pb AND Nd) SUPERCONDUCTOR CERAMICS VIA COPRECIPITATION AND THEIR ELECTROCHEMICAL CHARACTERISTICS

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By

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Chair: Prof. Zulkarnain Zainal, PhD

Faculty: Science

$ErBa_2Cu_3O_{7-\delta}$ is a type II high temperature superconductor, which is known as the 123-system. This type of superconductor is classified as the most stable high temperature superconductor. This dissertation presents the doping effect of diamagnetic elements (Zn and Pb) and paramagnetic elements (Ca and Nd) in the Er-123 System using the coprecipitation method as a procedure of synthesis. Electrochemical studies of free and doped samples have been done to emphasize the doping effect on the copper electrochemical behaviour in the superconductor.

A series of Zn, Ca, Pb, and Nd were successfully doped in the Er-123 system using the co-precipitation method. Metal acetates were used as starting materials, which were dissolved in acetic acid. The precipitating agent, oxalic acid in an alcoholic solution of

(water: iso-propanol) was used to form metal oxalates. Samples were dried and calcined for 24 hours at 900 °C before they were pressed into pellets and sintered for 24 hours at 920 °C. A second calcination and sintering period at 600 °C was applied for 2 and 3 hours, respectively. All heat treatments were carried out in the oxygen environment. The transport property of sintered samples was measured using the four-point probe electrical resistance measurement and AC Susceptibility. A scanning electron microscope and energy dispersive X-ray were used to identify the surface morphology and the chemical composition while the crystalline structure of the samples were determined using the X-ray diffraction (XRD) technique. Cyclic voltammetry was used to study the electrochemical behaviour in 0.1 M NH_4Cl as a supporting electrolyte.

The XRD pattern of the samples showed the presence of the secondary phase of 211 in the Zn-doped samples at $x \geq 0.15$ with 10-12 % peak intensity, while in the case of the Ca-doped samples a single-phase material was produced. Two phases of PbO_2 and Pb_3O_4 were produced for the Pb-doped sample, while for the Nd-doped, the Nd-123 phase was recorded at $x=0.15$. The orthorhombic phases of all doped samples are similar to the pure sample. Lattice parameters slightly change due to the replacement of the substituted element in the structure. In the case of the Zn and Ca-doped samples, the substitution occurred at the Cu site and the substitution in the Pb-doped and Nd samples occurred at the Ba and Er sites, respectively. The T_C values recorded were 85, 87, 85, and 91 K for 0.05 mole of doped Zn, Ca, Pb and Nd, respectively. These values decreased by 0.2 mole of dopant to 48, 68, 85 and 87 K.

The resistance versus temperature curve shows that the higher content of Zn in Zn-doped samples ($x \geq 0.15$) lowers the critical resistance temperature, T_C, below the liquid

nitrogen temperature. A semiconducting-like response appeared for the Zn-doped and Ca sample at a higher content of dopant ($x \geq 0.10$). Where in the Pb and Nd-doped samples, a typical superconducting curve was produced.

The microstructure study of the doped samples showed that the presence of the pores and boundaries between the grains reduced the T_C value due to the air pockets and the weak-links, which resist the current to flow. This effect increased by the content of the increase of dopant concentration in the sample.

The electrochemical study of the doped samples shows that the significant sensitivity depends on the pH and scan rate. The change of current has a semi-linear relationship with the acidity. The graph of current (I) versus scan rate (v) and current versus the square root of scan rate ($v^{1/2}$) were a straight line, which indicates that the electron transfer process is diffusion controlled and corresponds to an adsorption controlled process.

The diffusion coefficient values increased with the content of dopant where the values recorded at 0.05 and 0.2 mole of dopant were (7.45×10^{-5}, 8.67×10^{-5}), (8.67×10^{-5}, 1.07×10^{-4}) and (7.42×10^{-5}, 9.95×10^{-5}) cm^2/s for Ca, Pb and Nd, respectively, where the value of free doped sample ErBCO was 7.45×10^{-5} cm^2/s.

The value of charge increased by the content of doped element in the ErBCO system, where the recorded values were 808.01, 1230.91, 1042.92 and 990.61 $\mu C/cm^2$ with 0.2 mole of doped Zn, Ca, Pb and Nd respectively, where the undoped sample value was 497.25 $\mu C/cm^2$.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

SINTESIS SUPERKONDUKTOR SERAMIK $Er_{1-x}A_xBa_2Cu_3O_{7-\delta}$ (A=Ca,Zn, Pb, Nd) MELALUI KOPEMENDAKAN DAN CIRI ELEKTROKIMIA

Oleh

ELYAS SADEQ SULAIMAN AL-AGHBARI

Disember 2012

Pengerusi: Profesor Zulkarnain Zainal, PhD

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$ErBa_2Cu_3O_{7-\delta}$ ialah superkonduktor suhu tinggi jenis II, yang dikenali sebagai sistem 123. Superkonduktor ini dikelaskan sebagai superkonduktor suhu tinggi yang paling stabil. Disertasi ini menyajikan efek doping elemen diamagnetic (Zn dan Pb) dan elemen paramagnetik (Ca dan Nd) dalam Sistem Er-123 menggunakan metode kopresipitasi sebagai prosedur sintesis. Penelitian elektrokimia sampel bebas dan doped telah dilakukan untuk menekankan efek doping pada perilaku tembaga elektrokimia dalam superkonduktor.

Zn, Ca, Pb, dan Nd telah berjaya didopkan dalam sistem Er-123 dengan menggunakan kaedah ko-pemendakan. Logam asetat telah digunakan sebagai bahan permula, yang dilarutkan dalam asid asetik. Agen pemendakan asid oksalik dalam larutan beralkohol (air: isopropanol) digunakan untuk membentuk logam oksalate. Sampel dikeringkan dan kemudian dikalsinkan selama 24 jam pada suhu 900 ° C. Selepas itu, ia dijadikan pelet

dan dipanaskan selama 24 jam pada 920 ° C, di ikuti proses pemanasan kedua dan pensinteran pada 600 ° C selama 2 dan 3 jam. Kesemua rawatan haba dijalankan dalam persekitaran oksigen. Ciri pengangkutan sampel yang disinter diukur dangan menggunakan pengukuran rintangan empat titik pengukuran dan *susceptibility* ac. Mikroskop imbasan elektron (SEM) dan serakan tenaga sinar-X (EDX) telah digunakan untuk mengenalpasti morfologi permukaan morfologi dan komposisi kimia. Manakala fasa hablur sampel telah ditentukan dengan menggunakan teknik pembelauan sinar-X (XRD). Voltametri berkitar digunakan untuk mengkaji ciri elektrokimia dalam 0.1 M NH_4Cl sebagai elektrolit.

XRD menunjukkan kehadiran fasa sekunder 211 dalam sampel Zn yang didopkan pada $x \geq 0.15$, di mana bagi sampel terdop Ca hablur fasa tunggal terbentuk. Sebaliknya, terdapat dua fasa PbO_2 dan Pb_3O_4 dihasilkan dalam sampel terdop Pb, manakala fasa fasa Nd-123 yang terbentuk pada $x = 0.15$. Semua sampel yang didopkan menunjukkan fasa ortorombik sama seperti sampel tulen. Parameter kekisi setiap sampel adalah berlainan. Bagi sampel terdop Zn dan Ca penggantian belaku pada kedudukan Cu dalam sampel dan terdop Pb dan Nd penggantian berlaku pada tapak Ba dan Er. Nilai-nilai T_C tercatat adalah 85, 87, 85 dan 91 K untuk 0.05 mol doped Zn, Ca, Pb dan Nd, masing-masing. Nilai-nilai ini mengalami penurunan sebesar 0.2 mol dopan sampai 48, 68, 85 dan 87 K.

Hubungan antara rintangan dan suhu menunjukkan bahawa kandungan Zn sampel didopkan yang lebih tinggi ($x \geq 0.15$) mempunyai rintangan suhu yang lebih rendah dan kritikal, T_C, di bawah suhu cecair nitrogen. Respons seperti semipenghantar berlaku

dalam sampel terdop Zn dan Ca pada kandungan pendop yang tinggi ($x \geq 0.10$). Lengkungan tipikal superkonduktor dihasilkan untuk sampel terdop-Pb dan Nd.

Kajian mikrostruktur sampel terdop menunjukkan bahawa kehadiran liang dan sempadan antara bijirin merendahkan nilai T_C disebabkan oleh poket udara dan lekatan lemah yang menentang pengaliran arus. Kesan ini pertambah kerap dengan peningkatan pendopan sampel.

Kajian elektrokimia sampel terdop menunjukkan bahawa sensitiviti yang ketara bergantung kepada pH dan kadar imbasan. Perubahan arus mempunyai hubungan separa lurus dengan keasidan. Grafik arus (I) versus laju scan (v) dan arus versus akar kuadrat dari tingkat scan ($v^{1/2}$) adalah garis lurus yang menunjukkan bahwa proses transfer elektron adalah difusi dikendalikan dan sesuai dengan proses adsorpsi dikendalikan.

Nilai koefisien difusi yang meningkat dengan isi dopan dimana nilai tercatat sebesar 0,05 dan 0,2 mol dopan adalah (7.45×10^{-5}, 8.67×10^{-5}), (8.67×10^{-5}, 1.07×10^{-4}) dan (7.42×10^{-5}, 9.95×10^{-5}) cm^2/s untuk Ca, Pb dan Nd masing-masing, di mana nilai sampel gratis ErBCO doped adalah 7.45×10^{-5} cm^2/s.

Nilai biaya meningkat dengan kandungan unsur doped dalam sistem ErBCO, di mana nilai-nilai yang direkam adalah 808.01, 1230.91, 1042.92 dan 990.61 $\mu C/cm^2$ dengan 0.2 mol doped Zn, Ca, Pb dan Nd masing-masing, dimana nilai undoped sampel adalah 497.25 $\mu C/cm^2$.

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APPROVAL

I certify that an examination committee has met on **4.12.2012** to conduct the final examination of Elyas Sadeq Sulaiman Al Aghbari on his **Doctor of philosophy** thesis entitled "**Synthesis Of $Er_{1-x}A_xBa_2Cu_3O_{7-\delta}$ (A=Ca, Zn, Pb And Nd) Superconductor Ceramics Via Co-Precipitation And Their Electrochemical Characteristics**" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Doctor of Philosophy.

Members of the Examination Committee are as follows:

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This thesis submitted to the Senate of Universiti Putra Malaysia has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

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Date:

DECLARATION

I declare that the thesis is my original work except for the quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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ELYAS SADEQ SULAIMAN AL AGHBARI

Date: 4 December 2012

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