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Influence of Pr^{3+} substitution at Ba-site of $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ ceramic rods with hot-spot on oxygen sensing properties

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Abstract

In this work, we prepared $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ rods by the solid-state reaction method to investigate the influences of changes in structure and the expected decrease in average Cu valence on oxygen sensing properties of self-heating rods with hot-spots. X-ray powder diffraction analysis showed that orthorhombicity of the structure reduces with increasing Pr^{3+} concentration. After the hot-spot became visible, samples $x=0$ and $x=0.05$ showed a sudden drop in current before remaining constant with increasing voltage. This is suggested to be due to steep increase in resistivity caused by the sudden increase in temperature of the hot-spot together with the structural changes that lead to reduction in oxygen content. However, for the $x=0.25$ and $x=0.4$ rods the output current shows no sudden drop. Our results also showed that the reduced magnitude of the output current with increasing Pr^{3+} could be attributed to the reduction in intrinsic hole concentration. The output current for all samples showed strong dependence on pO_2. Although the sensitivity of the output current to pO_2 between 50% pO_2 and 100% pO_2 reduces with increasing x, the stability and repeatability of the output current seem to improve. Also, while substitution of Pr^{3+} reduces the magnitude of the output current, it produces a better response time toward different pO_2.

Keywords: C. Electrical properties; D. Oxide superconductors; E. Sensors

1. Introduction

Quite recent studies have shown that rods of RE123 ceramics popularly known as superconducting material, were found applicable in oxygen sensing without the need of any external heater where the output current, defined as the current in equilibrium state after appearance of a hot-spot, is dependent on oxygen partial pressure, pO_2 [1–4].

The oxygen sensing property of RE123 hot-spot can be explained in terms of absorption of oxygen gas by the hot-spot before dissociating into oxide ions and holes. The overall reaction of ionic conduction is expressed as

$$O_2 \leftrightarrow 2O^{2-} + 4H^+ \quad (1)$$

The relationship between conductivity, σ and pO_2 based on Eq. (1) using mass action law is given by

$$\sigma \propto pO_2^{1/6} \quad (2)$$

Eq. (2) shows the dependency of the output current on pO_2 where the slope of log output current versus log pO_2 curve indicates the overall reaction of ionic conduction as depicted in Eq. (1).

Interestingly while previous study on Gd123 [1] showed a sudden drop in current upon the appearance of hot-spot, a study on Eu123 on the other hand, reported that when Ca^{2+} was substituted at Eu-site, current shows no sudden drop but displays an almost constant current plateau behavior [4]. The sensitivity of the output current to oxygen for the Eu123 rods however reduces when Ca^{2+} was substituted at Eu site. On the other hand, a study on the substitution of Sr at Ba site for Ho123 rods shows higher sensitivity of output current to pO_2 below 40% than above 40% pO_2 [3]. As such, elemental substitution in RE123 compound at RE-site and Ba-site, may result in better stability and repeatability of output current and has the potential to reduce the sudden drop in output current [3,4].

Further study by Hassan and Yahya [2] showed that the hot-spot temperature played an important role in the stability of the output current which was stable above 700 °C.

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It was suggested that structural changes from orthorhombic to tetragonal occur around 700 °C and the sensitivity of output current was reduced as the structure changed to tetragonal [3].

On the other hand, previous studies by Xu et al. [5] and Klencsar et al. [6] on $EuBa_{2-x}Pr_xCu_3O_{7-\delta}$ showed that Pr substitution, besides reducing intrinsic hole concentration, can induce structural change from orthorhombic ($x < 0.3$) to tetragonal ($x > 0.3$) at room temperature. Because the structural change can affect oxygen activation energy [9], therefore it is interesting to study the effect of Pr^{3+} substitutions at Ba-site on oxygen sensing, stability and sensitivity of output current in different concentrations of pO_2.

In this paper, $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ (x=0–0.40) ceramics were synthesized and sensor rods were fabricated. *I–V* characteristic, oxygen sensing properties and sensitivity were investigated for pO_2 from 20% to 100%.

2. Experimental details

The $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ (x=0, x=0.05, x=0.25 and x=0.40) samples were synthesized by the conventional solid-state-reaction method. High purity oxide powders of Eu_2O_3, $BaCO_3$, CuO and Pr_6O_{11} were mixed and then ground for 2 h in an agate mortar. The mixture was calcined at 950 °C for 24 h in a box furnace followed by regrinding for 2 h in an agate mortar. The calcination process was repeated and the mixture was reground and pressed into pellets and sintered at 950 °C in a box furnace for 24 h. $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ rods were fabricated by cutting the pellets into rectangular rods with dimensions of around 13 mm × 0.65 mm × 0.65 mm.

Powder X-ray diffraction (XRD) was carried out using the Rigaku model D/MAX 2000 PC with Cu-K_α radiation to confirm the samples' structure. *I–V* characterization of the sensor rod before and after appearance of the hot-spot was conducted in a chamber at 1 atm of pO_2 from 20% to 100%.

3. Results and discussions

The X-ray diffraction patterns showed that all samples were crystalline and single phased Eu123 compounds with orthorhombic structure and space group *Pmmm*. Table 1 shows the lattice parameters, resistivity, ρ(300 K), unit cell volume, v and orthorhombicity for all samples. The effect of the substitution on the structure was in good agreement with previous studies [5–7]. The orthorhombicity of the x=0.25 and x=0.40 rods were much reduced with having structures considered as pseudo-tetragonal form. In addition, resistivity at room temperature (Table 1) increased with increasing x which indicates that the hole concentration reduces with increasing Pr^{3+} substitution [10].

Fig. 1 shows the *I–V* graph at room partial pressure for samples x=0–0.40. The current linearly increases with V in the low voltage region for x=0, x=0.05 and x=0.25, but for x=0.40 the current only starts to increase at the higher voltage region above 3 V. After certain applied voltage when the hot-spot starts to appear, V_c, current drops suddenly for x=0 and x=0.05 and then remained relatively constant. However, for x=0.25, there was no sudden drop in current. Interestingly, for x=0.40, before the appearance of hot-spot, a sudden jump in current was observed which then remained fairly constant after a hot-spot became visible. In addition, the magnitude of the stable output current decreases as x increases indicating that it is affected by the Pr^{3+} substitution. In order to maintain charge balance as the amount of Pr^{3+} substituted at Ba-site increases, the Cu valence is expected to decrease [10] and consequently this reduces the amount of intrinsic holes and this leads to the decrease in the output current. As more Pr^{3+} is substituted, V_c shifts toward higher voltage indicating more energy (joule heating) is needed for the hot-spot to be visible.

Fig. 2 shows *I–V* and *T–V* graphs for (a) x=0.05 and (b) x=0.25 rods in ambient concentration of pO_2. Fig. 2(a) shows that a sudden rise in temperature at the hot-spot region coincides with a sudden drop in current at V_c for both x=0 and x=0.05. The observed abrupt drop in the current at around 400 °C is suggested to be due to the steep increase in resistivity caused by the suddenly increased hot-spot temperature. The increase of resistivity is suggested to be due to reduction in oxygen content [10] which starts to deplete around 400 °C [8] as a result of structural changes from orthorhombic to tetragonal. The current is then stabilized as the applied voltage approaches around 3.5 V probably due to the heat generated, $J^2\rho$ by the hot-spot matching the amount of heat released, W [1]. Interestingly, for x=0.25 (Fig. 2b)), after the appearance of hot spot, the temperature at the hot spot region shows no sudden rise and as a result the current shows no sudden drop but instead a constant-current plateau was immediately observed. The x=0.25 and x=0.40 rods which were in pseudo-tetragonal form at room temperature are suggested to change swiftly to purely tetragonal structure when the temperature reaches around 400 °C. The lower current density, J leads to a lower generated heat, $J^2\rho$, for the x=0.25 sample and it balances the dissipated heat, W much quicker than the other samples (x=0 and x=0.05) resulting in formation of the constant-current plateau [1].

Fig. 3(a) shows the output current with different pO_2 for x=0, x=0.05 and x=0.25. Results show good agreement with Takata et al. [1], where the output current depends on pO_2. In general, output current of x=0 and x=0.05 are more sensitive to pO_2 than that of x=0.25. The slopes of the graphs however indicate that all the rods are more sensitive from 20% to 40% pO_2 than from 50% to 100% pO_2. Significant changes of output current from 20% to 40% pO_2 could be due to the fact that at very low pO_2, (20% pO_2) only nominal extrinsic holes were generated resulting in lower output current as compared to 40% pO_2. Moreover, it was reported from previous study on $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ superconductors [6] that the lattice structure can accommodate higher oxygen content

Table 1
Lattice parameters, a, b, c, volume, v, resistivity, ρ(300 K) and orthorhombicity, $(b-a)/(a+b)$ for $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ with (a) $x=0$, (b) $x=0.05$, (c) $x=0.25$ and (d) $x=0.40$.

Parameters	Pr^{3+} contents (x)			
	(a) 0.00	(b) 0.05	(c) 0.25	(d) 0.40
ρ (Ω cm)	0.0716(4)	0.0700(3)	0.4193(6)	7.9705(6)
a (nm)	0.3858(1)	0.3557(2)	0.3685(1)	0.3499(1)
b (nm)	0.3622(2)	0.3678(3)	0.3684(2)	0.3496(2)
c (nm)	1.1669(3)	1.1705(5)	1.1666(3)	1.1631(5)
v (nm^3)	0.1630(2)	0.1531(3)	0.1584(2)	0.1423(2)
$(b-a)/(a+b)$	0.0315(5)	0.0167(4)	0.0001(0)	0.0004(0)

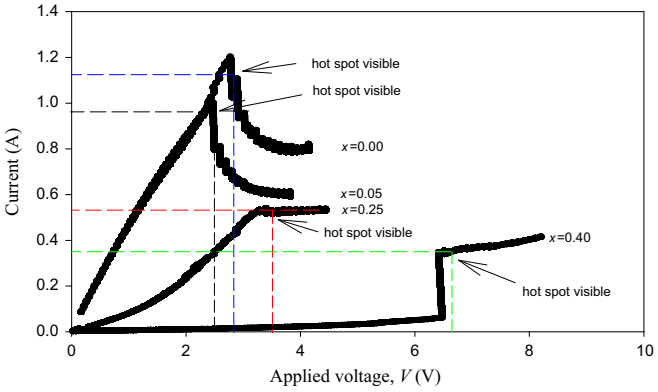

Fig. 1. I–V graph for $x=0$, $x=0.05$, $x=0.25$ and $x=0.40$. The dashed lines indicate the point where the hot-spot starts to become visible at room partial pressure.

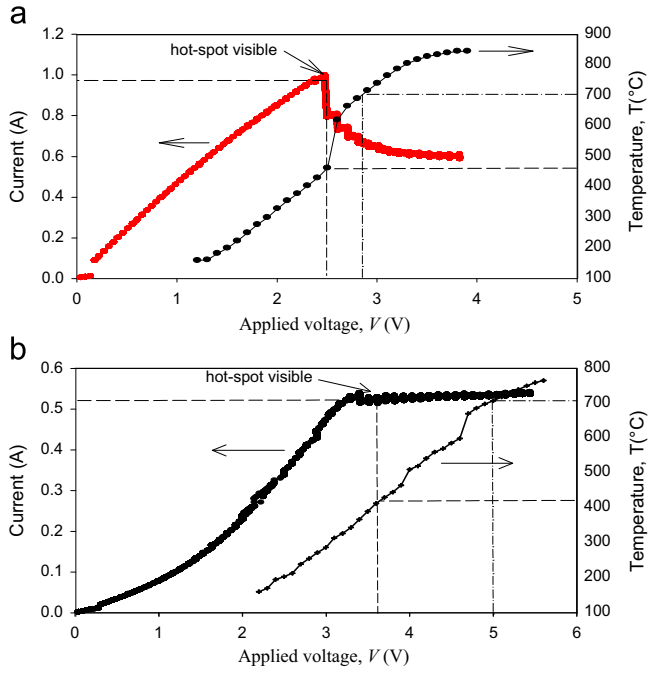

Fig. 2. I–V and T–V graphs for (a) $x=0.05$ and (b) $x=0.25$. The dashed line indicates V_c and the dashed–dotted line indicates the point where the temperature reaches 700 °C.

at lower Pr compared to higher Pr concentration. As such, it is possible that at low Pr content ($x=0$ and $x=0.05$) the structure was able to absorb more oxygen compared to the

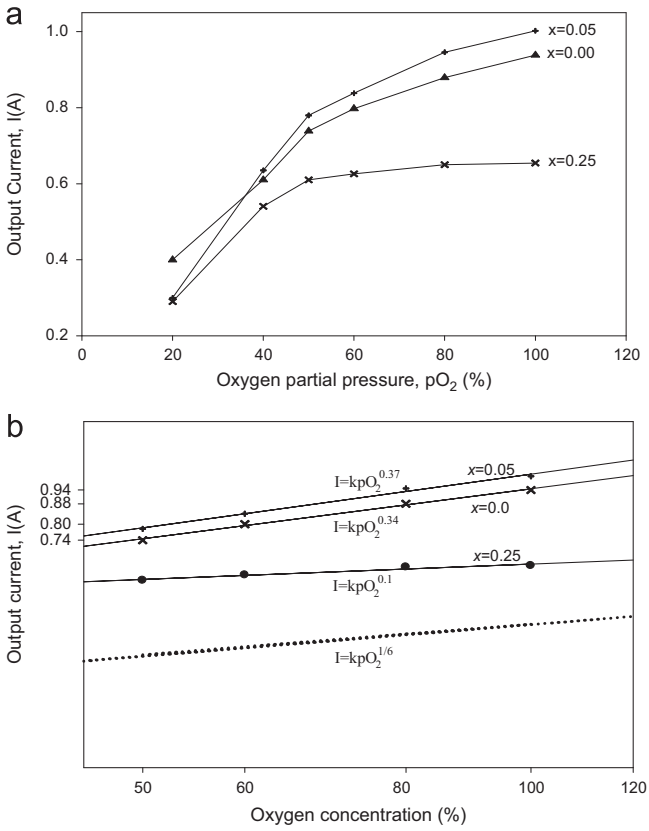

Fig. 3. (a) Graph of output current, I at different oxygen partial pressures, pO_2 and (b) graph of output current versus pO_2 at high concentration of oxygen partial pressure, pO_2 plotted on a log scale. Dotted lines indicate the ideal slope of the proportionality of σ to $pO_2^{1/6}$.

rod with higher Pr content ($x=0.25$). This leads to higher oxygen dissociation into holes which caused a bigger change in output current with increasing pO_2 and thus contribute to the higher sensitiveness for lower Pr. Besides, the higher sensitivity for oxygen absorption between 20% and 40% pO_2 is probably related to the lower initial oxygen content of the tetragonal structure. However at pO_2 concentration above 50%, the oxygen content reaches a saturation level and hence leads to the reduced sensitivity. Fig. 3(b) is the graph of output current versus pO_2 on a log scale. Above 50% pO_2, rod with $x=0.25$ deviates below than the ideal slope of 1/6 as depicted by Eq. (2) compared with other rods ($x=0$ and $x=0.05$). Our analysis using the mass action law on the slope

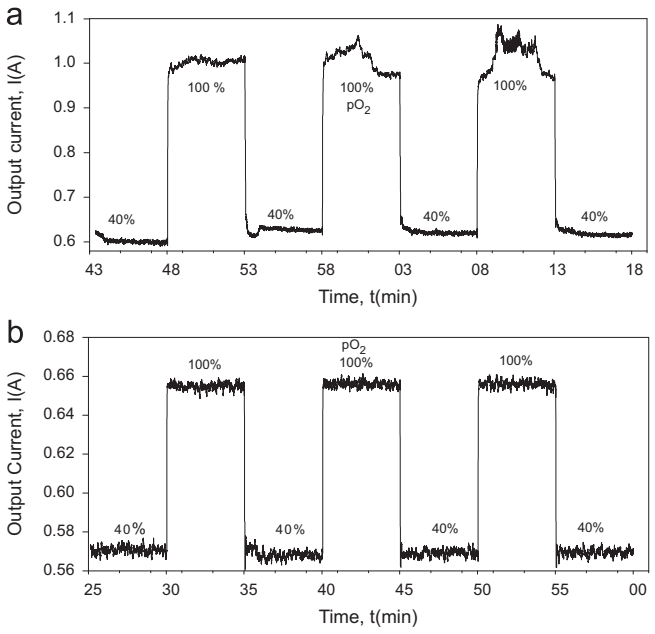

Fig. 4. Repeatability of output current between 40% pO_2 and 100% pO_2 for (a) $x=0$ and (b) $x=0.25$ at around 4 V.

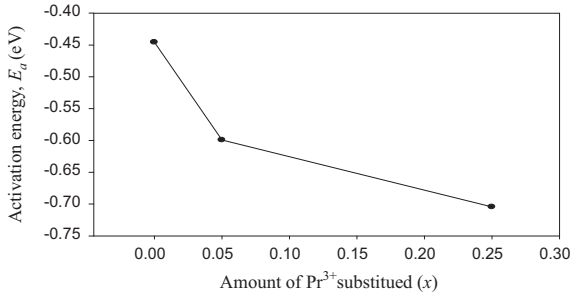

Fig. 5. Graph of activation energy, E_a (eV) versus amount of Pr^{3+}.

change indicates Cu^{3+}(holes) is reduced during ionization of oxygen and this supports our earlier suggestion that the hole concentration is reduced with Pr^{3+} substitution.

Fig. 4 shows the repeatability of the output current to changes in oxygen partial pressure for (a) $x=0$, (b) $x=0.05$ and (c) $x=0.25$, respectively, from 40% pO_2 to 100% pO_2. It can be seen that the Pr^{3+}-free sample shows instability in output current compared to the Pr^{3+} substituted $x=0.25$ rod.

The absorption rate depends on temperature, T and can be described using the Arrhenius law behavior for temperature, T dependence of respond time, t_{res} as below:

$$t_{res} = t_o \exp\left(\frac{E_a}{k_B T}\right) \quad (3)$$

where t_{res} is the time taken for the output current to reach saturated level, t_o is a constant independent of temperature, T, E_a is the activation energy of ionic migration and k_B is the Boltzmann constant [2]. Each time oxygen partial pressure changes from 40% pO_2 to 100% pO_2 and vice versa, absorption and desorption processes take place, respectively. As the amount of Pr^{3+} substitution at Ba-site increases, the saturated output current level was reached faster (Fig. 4), indicating that the response time, t_{res} is reduced. The value of E_a was computed using Eq. (3) for response time measured at hot-spot temperature of 640 °C and it was found that E_a decreased with increasing Pr^{3+} substitution (Fig. 5). The lower E_a with Pr-substitution, facilitates oxygen absorption and desorption and this is suggested as the reason for the improved stability and repeatability of the output current.

4. Conclusions

The effect of Pr^{3+} substitution at Ba-site on oxygen sensing of $Eu(Ba_{1-x}Pr_x)_2Cu_3O_{7-\delta}$ rods with hot-spot was studied. The Pr^{3+} substitution was able to modify the output current after formation of hot-spot from a sudden drop (for $x=0$ and $x=0.05$) to a constant current plateau behavior (for $x=0.25$). The prevention of the sudden drop in output current is suggested to be due to the lower current density that caused the generated heat to be able to rapidly match the dissipated heat. The $x=0$ and $x=0.05$ rods showed higher sensitivity for pO_2 above 50%, but the $x=0.25$ rod showed lower oxygen activation energy, E_a, faster response time and improved stability and repeatability of output current.

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