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# High temperature oxygen sensing properties of oxygen deficient $RBaCo_2O_{5+\delta}$ thick films

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ABSTRACT

$RBaCo_2O_{5+\delta}$ (R = Sm, Eu, Dy, Gd, and Y) thick films were prepared by the solid state reaction followed by the spin-coating method. The oxygen resistivity sensor properties of these films were investigated in switching $O_2/N_2$ atmosphere. The results show that the $RBaCo_2O_{5+\delta}$ films are promising as oxygen resistance sensors at elevated temperature. Especially, $DyBaCo_2O_{5+\delta}$ film shows a fast response speed, high sensitivity and good repeatability at 600 °C. The correlation between the sensor properties of $RBaCo_2O_{5+\delta}$ thick films and their oxygen intake/release properties is also discussed.



## 1. Introduction

Oxide materials are widely used as gas sensors due to the sensitivity of their electrical conductivity to surrounding atmosphere. For example, the electrical properties of metal oxides $SnO_2$ and ZnO can be changed by surrounding atmosphere. They have been used as sensors to detect combustible and noxious gases. However, in order to meeting the requirement of rapid development of industry and environmental protection more advanced sensor materials are needed, especially those with high selectivity and stability as well as special functions. For instance, in order to achieve complete combustion of gasoline, oxygen sensors that can stand for high temperature and chemical erosion in the tail gas of automobiles are indispensable.

Oxygen-nonstoichiometric oxides with perovskite-like structure have fast interior oxygen diffusion and oxygen intake/release when surrounding temperature or oxygen partial pressure are changed, and therefore have been employed in oxygen separation or gas purification, electrode and electrolyte materials in solid oxide fuel cells (SOFC), oxygen permeation membranes as well as oxygen sensors [1–4]. Recently, the oxygen-deficient double layers perovskite-like oxides $RBaM_2O_{5+\delta}$ (abbreviated as R112, where R = Y and rare-earth elements, M = Co, Fe, and Mn, $0 \le \delta \le 1$), have attracted much attention because of their unique electric and magnetic properties. The crystal structure of these oxides can be regarded as a layered crystal $A'A''B_2O_6$ by doubling the unit cell of standard perovskite structure, and consists of consecutive layers $[MO_2]$–[BaO]–$[MO_2]$–$[RO_\delta]$ stacked along the *c*-axis [5,6]. The amount of oxygen ions in the $RO_\delta$ layer can be easily controlled in the range of $0 \le \delta \le 1$ by annealing the samples in appropriate atmosphere and temperature. The saturated oxygen content increases with the increase in the $R^{3+}$ ion sizes [5–7]. The widely allowed variation of oxygen content leads to several types of superstructure with different oxygen atom arrangement in the $RO_\delta$ layer. Some interesting properties were reported such as charge ordering [8,9], metal–insulator transition [10,11], orbital order [12], large thermoelectric power [13,14], and remarkable oxygen storage capability [15].

Taskin et al. [16] compared the oxygen diffusion behavior of the double layered $GdBaMn_2O_{5+\delta}$ and the simple cubic $Gd_{0.5}Ba_{0.5}Mn_2O_{5+\delta}$, and found that the oxygen ion diffusion rate can be enhanced by several orders of magnitude if a simple cubic structure was transformed into a double layered structure. The reason is that the double layered structure can reduce the oxygen bonding strength and provide disorder-free channels for oxygen ions moving. Hao et al. [17], investigated the oxygen intake/release behavior of R112 (Pr112, Gd112, and Y112) in a high temperature range, and estimated the oxygen intake/release rate constants $k_a$, $k_d$ as well as oxygen permeation flux $J_{O_2}$. Kim et al. [18,19] reported that $PrBaCo_2O_{5+\delta}$ thin films have unusually rapid oxygen ion diffusion and surface exchange kinetics at low temperature (300–500 °C). The rapid interior oxygen diffusion of the R112 oxides suggests their potential applications in fields requiring fast oxygen diffusion, such as oxygen permeation membranes [20–22] and cathode

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**Table 1**
Lattice constant a, b, c, and unit cell volume V of R112 films.

| Parameters | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
|---|---|---|---|---|
| Y112 | 3.87 | 3.87 | 7.49 | 112.0 |
| Dy112 | 3.88 | 3.88 | 7.51 | 113.2 |
| Gd112 | 3.89 | 3.89 | 7.53 | 113.9 |
| Eu112 | 3.91 | 3.89 | 7.55 | 114.8 |
| Sm112 | 3.92 | 3.89 | 7.57 | 115.4 |

materials in SOFC [23,24]. However, studies on applications of R112 oxides as oxygen sensors are rare. So far, only transport properties of La112 thin film under reducing-oxidizing environment were reported [25]. Therefore, in this paper, we present our study on the oxygen sensor properties of $RBaCo_2O_{5+\delta}$ (R = Sm, Eu, Dy, Gd, and Y). We made R112 thick films and investigated their electrical resistance variation when oxygen partial pressure was changed in surrounding atmosphere.

## 2. Experimental

$RBaCo_2O_{5+\delta}$ oxides were prepared by the solid state reaction method using $R_2O_3$ (R = Sm, Eu, Dy, Gd, and Y; Aladdin, 3–5 μm, 99.99%), $BaCO_3$ (Wu Zhou, ~1.5 μm, ≥99.8%), and $Co_3O_4$ (Kermel, 4–10 μm, ≥98.5%) as starting materials. The stoichiometric mixtures of the starting materials were ground thoroughly in an agate mortar. After decarbonising at 1000 °C, the mixtures were pressed into pellets and heated at 1100 °C for 20 h in air, and then slowly cooled down to room temperature. Then the pellets were ground into powders (average particle size of 1.4 μm) for the use to make thick films.

$RBaCo_2O_{5+\delta}$ (R = Sm, Eu, Dy, Gd, and Y) thick films using $Al_2O_3$ plates (15 mm × 15 mm × 0.5 mm) as substrate were prepared using the spin-coating method. A paste consisting of 23 wt% R112 powder, 43 wt% of glycerol, 4 wt% of a glycol and 30 wt% of ethanol was spin-coated on $Al_2O_3$ substrate at 3000 rpm for 30 s using a spin-coating apparatus (Model KW4A, IMECAS, China). Then the obtained films were dried at 50 °C for 60 min, and finally annealed at 1100 °C in air for 30 min. X-ray diffraction (XRD, X'pert Pro PANalytical, Holand, using Cu-Kα radiation (λ = 1.5406 Å)) analysis was carried out to check the phase structures of the films. The crystal constants for R112 phase with different rare earths were calculated through a least-square method by using the XRD data. The microstructure and film thickness were observed using a field-emission scanning electron microscopy (SEM, 15 kV, JSM-6700F, JEOL, Japan). Samples with length 15 mm and width 6.0 mm were cut from the annealed $Al_2O_3$ substrate films for electrical measurement. The electrical resistance of the R112 films was measured by using the standard four-probe method on a lab-made apparatus (using a 2400 source meter to apply alternation current and a 2182 multimeter (KEITHLEY, USA) to collect voltage controlled by a computer) in a tube furnace with $O_2$ or $N_2$ gas flow to measure the change of the electrical resistance with the change of temperature or surrounding oxygen pressure. The electrical resistivities of the films were calculated by the measured resistance, the distance $L$ between two voltage poles, the film width $W$. The film resistivity in this paper refers to area specific resistivity defined as $\rho = RW/L$, where $R$ is the measured resistance of the film.

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the $RBaCo_2O_{5+\delta}$ (R = Sm, Eu, Dy, Gd, and Y) thick films. All R112 patterns can be indexed to single "112" phase. Their lattice parameters are listed in Table 1. It can be seen that the lattice parameters decrease with the decrease in the size of $R^{3+}$ ions. The SEM image in Fig. 2 shows the microstructure

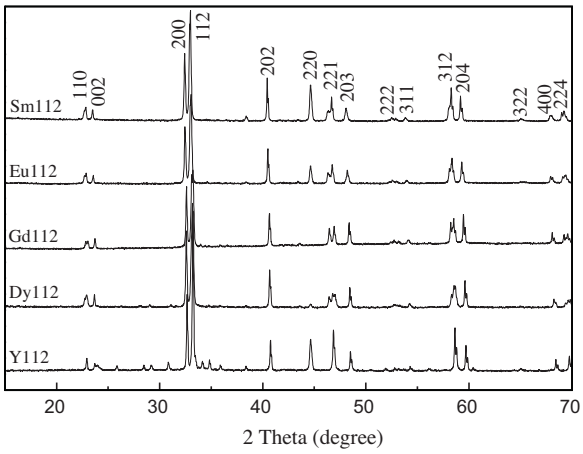


**Fig. 1.** XRD patterns of R112 thick films.

of a typical thick film of Y112. All the other R112 films have similar morphology and not shown here. It can be seen that the film is consist loosely of grains with grain size of 1–5 μm. Such microstructure will increase the electrical resistivity of the film as compared with the bulk sample, but it is beneficial to the oxygen sensor applications since it can lead to fast oxygen intake or release when the oxygen partial pressure in surrounding atmosphere is changed.

The temperature dependence of resistivities of films measured from room temperature to 600 °C in air is presented in Fig. 3. It can be seen that the resistivities of all films decreases with the increase in temperature, indicating typical semiconductor behavior. This is consist with the reported behavior of $LaBaCo_2O_{5-\delta}$ and $GdBa_{0.5}Sr_{0.5}Co_2O_{5+\delta}$ films [25,26]. The electrical resistance of R112 will change with its oxygen constant and this is the basis for their using as oxygen sensors. Fig. 4 shows a typical isothermal thermogravimetry (TG) curve of Gd112 at 700 °C under switching $O_2/N_2$ gas flow. When $O_2$ flow is switched to $N_2$ flow oxygen will be released (desorbed) from the sample [17] and the mass of the sample will be reduced. When from $N_2$ flow to $O_2$ oxygen will be intaken (adsorbed) by the sample and the mass of the sample will be increased. The oxygen intake/release will change the carrier concentration and result in a change of the electrical resistance [14,24]. The effect of oxygen release on the carrier concentration can be understood from the defect chemistry of the perovskite oxides. The resistivity is related to the oxygen vacancy concentration $[V_O^{\bullet\bullet}]$ in the crystal. The release/intake of oxygen can be represented by $O_O^x \Leftrightarrow \frac{1}{2}O_2 + [V_O^{\bullet\bullet}] + 2e$. Thus, the release (intake) of oxygen

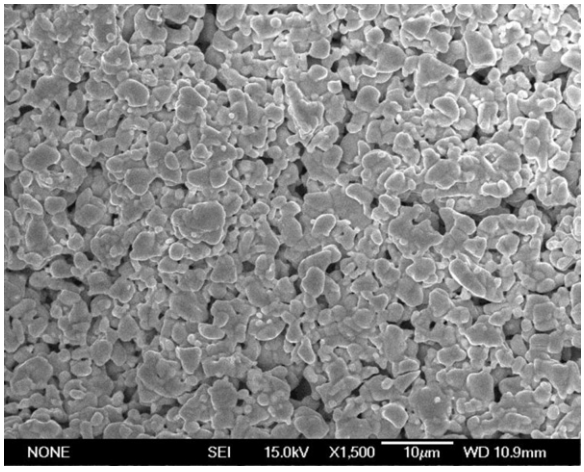


**Fig. 2.** Microstructure of Y112 thick films.