

Co 掺杂的 $\text{YBa}_2\text{Cu}_2\text{O}_{6+\delta}$ 的 氧非计量和氧渗透性能研究*

郑翠红, 杨萍华**, 刘 卫, 陈初升

(中国科学技术大学材料科学与工程系, 合肥 230026)

摘 要: 研究钴离子部分取代铜离子对 $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ 的氧非计量值 δ 和氧渗透率的影响. 对于钴替代的样品, 氧非计量的绝对值变大, 且其数值不再随温度和氧分压的变化发生显著变化. $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ 样品在中、高温具有可观的氧渗透率. 对于厚度为 1.2 mm 的致密 $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ 样品, 在 850°C 时, 只要在样品两端施加较小的氧分压差 ($P_{\text{O}_2} = 21.2 \text{ kPa}$, $P_{\text{O}_2} = 101 \text{ Pa}$), 其氧渗透率即可达 $57 \mu\text{mol}/\text{cm}^2 \text{ s}$, 明显高于 $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ 的氧渗透率 ($31 \mu\text{mol}/\text{cm}^2 \text{ s}$). $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ 的高氧渗透率在结构上可被归结为位于晶胞基面上的氧离子和氧空位的均匀分布.

关键词: $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$; 氧非计量; 氧渗透; 扩散

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Oxygen Nonstoichiometry and Permeability of Co-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ *

Zheng Cuihong, Yang Pinghua**, Liu Wei, Chen Chusheng

(Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026)

Abstract The effects of substitution of Cu by Co in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ on the oxygen nonstoichiometry and permeability were investigated. The oxygen nonstoichiometry δ increased as a result of Co substitution, and its values did not change very much with the changing temperature and oxygen partial pressure. An oxygen permeation flux of $57 \mu\text{mol}/\text{cm}^2 \text{ s}$ was observed at 850°C from $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ disk-shaped dense sample of thickness 1.2 mm with one side exposed to air ($P_{\text{O}_2} = 21.2 \text{ kPa}$) and the other side to flowing helium ($P_{\text{O}_2} = 101 \text{ Pa}$), but only $31 \mu\text{mol}/\text{cm}^2 \text{ s}$ was measured for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. The improved oxygen permeability in $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ was attributed to the even distribution of oxygen ions and oxygen vacancies in the basal plane.

Key words $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$, Oxygen nonstoichiometry, Oxygen permeability, Diffusion

1 Introduction

$\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ oxide exhibits significant oxygen nonstoichiometry and fast oxygen transport kinetics at

elevated temperatures^[1]. These properties are of great importance to fine-tune its superconductivity. The fast oxygen transport kinetics also presents a possibility to separate oxygen from the air by using a membrane

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** Corresponding author, E-mail: pxyang@ustc.edu.cn Received 5 June 2003; in final form 27 September 2003.

made from the oxide^[21].

The oxygen transport in $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ is believed to take place in the basal plane CuO_δ of the lattice^[1, 21]. It is known that the oxygen content in the basal plane can increase through the substitution of Cu with Co^[3]. This work was mainly to examine the effects of the substitution on the oxygen content and the permeation properties.

2 Experimental

$\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ samples were prepared by the solid state reaction technique. Appropriate amounts of AR grade powders Y_2O_3 , BaO , Co_2O_3 and CuO were weighed and thoroughly ground. The mixed powder was placed in an alumina crucible, heated up to 930°C and maintained at that temperature for 24 h, then the furnace was cooled to the room temperature; this process was repeated twice. The as-obtained powder was pressed into compacts and sintered to denseness at 950°C for 24 h. The sintered compact reached a relative density over 90%.

Sintered samples were annealed at temperatures of interest for 24 h under controlled oxygen partial pressure and then quenched by transferring them from inside a furnace to a cold copper plate. Oxygen nonstoichiometries of the quenched samples were determined using a modified double iodometric titration technique^[4, 5].

For the oxygen permeation measurement, a permeation cell was formed by sealing a disk-shaped sample of thickness 1.2 mm and a diameter of 12 mm to an alumina tube using a glass ring. Air was led over one side of the sample as feed gas, while at the other side a helium stream of high purity was introduced to sweep away the permeated gas which then was analyzed by an online gas chromatography^[6].

3 Results

3.1 Oxygen nonstoichiometry

The oxygen nonstoichiometries (δ) of both $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ samples that had been annealed at 600, 700, 800 and 900°C under controlled oxygen partial pressure were determined using

the iodometric titration technique. It can be seen from Fig. 1 that the value of δ for the Co-substituted sample was significantly higher than that for the un-substituted sample. For the substituted sample annealed in air atmosphere, δ took a value of 0.95 at 900°C and 1.12 at 600°C , whereas 0.27 and 0.67 for the un-substituted sample. It can also be seen that decreasing oxygen partial pressure led to a decrease in the oxygen content, but this effect was less pronounced for the substituted sample. When subjected to a low oxygen partial pressure of 1 kPa, the substituted sample took a value of 0.85 for δ at 900°C and 1.06 at 600°C , whereas 0.17 and 0.29 for the un-substituted sample.

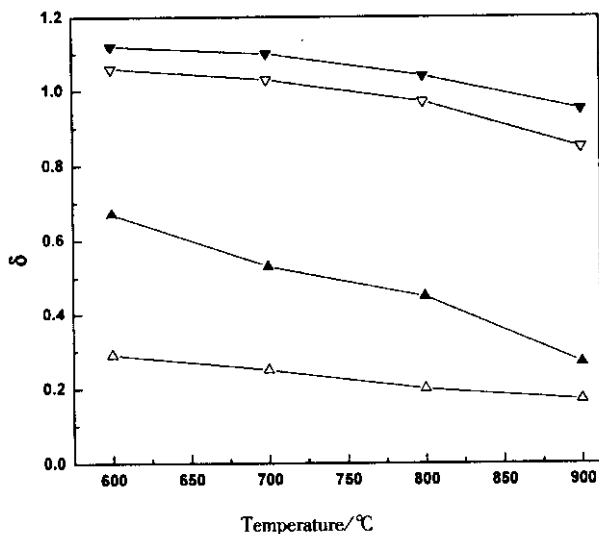


Fig. 1 Oxygen nonstoichiometry as a function of annealing temperature ($\nabla, \blacktriangledown$) $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and (Δ, \blacktriangle) $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

The filled symbol denotes samples exposed to air $p_{\text{O}_2} = 21.2$ kPa) and open ones in contact with atmosphere of $p_{\text{O}_2} = 101$ Pa.

3.2 Oxygen permeation

Oxygen permeation fluxes through disk-shaped samples were measured in the temperature range of $850 \sim 640^\circ\text{C}$ with the oxygen partial pressure at the feed side 21.2 kPa and 101 Pa at the permeated side. As can be seen in Fig. 2, the substitution of Cu with Co in the basal plane resulted in improved oxygen permeability. The oxygen flux for $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ was $57 \mu\text{mol}/\text{cm}^2\text{s}$ at 850°C under a relatively small oxygen partial pressure gradient, which was much higher than that of $31 \mu\text{mol}/\text{cm}^2\text{s}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$. The other effect of the Co-substitution was the increase of ap-

parent activation energy for the permeation process , which was (64.5 ± 0.4) kJ/mol for $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and (43.8 ± 0.6) kJ/mol for $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$.

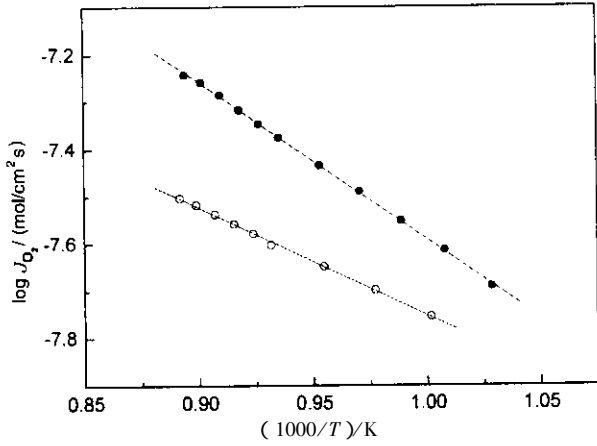


Fig. 2 Temperature dependence of oxygen permeation flux through 1.2 mm thick disk-shaped samples
(●) $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and (○) $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

4 Discussion

The oxygen permeation through $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ -based materials involves counter-transport of oxygen ions along the CuO_δ basal plane and electrons along CuO_2 planes in the lattice. The oxygen permeation flux can be described by^[7]

$$j_{\text{O}_2} = -\frac{1}{(4F)^2} \frac{\sigma_{\text{ion}}\sigma_{\text{el}}}{\sigma_{\text{ion}} + \sigma_{\text{el}}} \nabla \mu_{\text{O}_2} \quad (1)$$

where F is the Faraday constant , σ_{ion} the oxygen ionic conductivity , σ_{el} the electronic conductivity , and $\nabla \mu_{\text{O}_2}$ the gradient of oxygen chemical potential gradient. With the Nernst-Einstein relationship , σ_{ion} can be expressed as

$$\sigma_{\text{ion}} = \frac{C_0 D_s Z_0^2 F^2}{RT} \quad (2)$$

where C_0 is the concentration of the mobile oxygen ions with the valence charge $Z_0 = -2$, D_s the self-diffusion coefficient which follows that

$$D_s = P_V D^0 \exp(-E_m/RT) \quad (3)$$

where P_V is the probability of the oxygen lattice site being vacant , i. e. , occupied by an oxygen vacancy , D^0 is the pre-exponential factor and E_m is the activation energy barrier for oxygen migration.

For the $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ -based materials , the oxygen ionic conductivity is much smaller than the electronic conductivity ($\sigma_{\text{ion}} \ll \sigma_{\text{el}}$). Since the transport of oxygen ions only takes place along the basal plane , thus $C_0 = \delta/V_m$, where V_m is the molar volume , $P_V = (1 - \delta/2)$; $\nabla \mu_{\text{O}_2}$ can be expressed as $RT \frac{\partial \ln p_{\text{O}_2}}{\partial x}$. Combination of Eqs. (1) ~ (3) yields

$$j_{\text{O}_2} = -\frac{\delta}{4V_m} \left(1 - \frac{\delta}{2}\right) D^0 \exp\left(-\frac{E_m}{RT}\right) \frac{\partial \ln p_{\text{O}_2}}{\partial x} \quad (4)$$

It is clear from Eq. (4) that an even distribution of oxygen ions and oxygen vacancies in the basal plane , i. e. , the term $\delta \left(1 - \frac{\delta}{2}\right)$ achieving the highest value of 0.5 , is desirable for the oxygen transport. Fig. 3 gives the value of the term at different temperatures , in which the mean values of δ in the p_{O_2} range of 209 and 1 kPa are used. As can be seen from Fig. 3 , for the substituted sample , the term $\delta \left(1 - \frac{\delta}{2}\right)$ retains a desired value of ~ 0.50 over a wide range of temperatures ; but for the un-substituted sample , the value is 0.23 and 0.36 at 900 and 600°C , respectively. The difference in the value of $\delta \left(1 - \frac{\delta}{2}\right)$ between the substituted and un-substituted samples can partly account for the difference in the oxygen permeability.

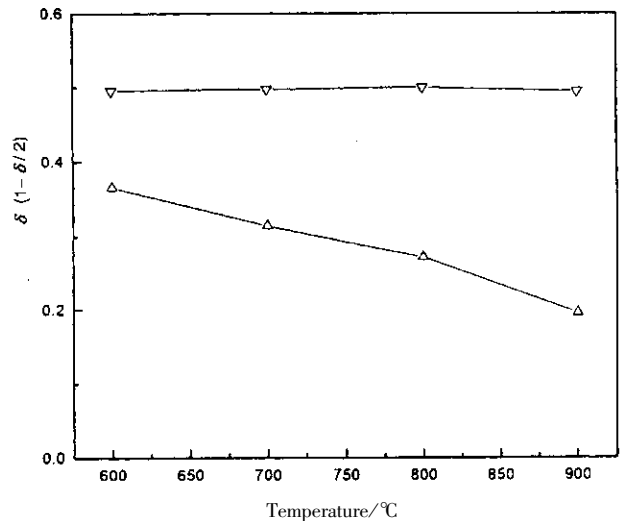


Fig. 3 $\delta \left(1 - \frac{\delta}{2}\right)$ vs. temperature in (▽) $\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ and (Δ) $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$

Eq.(4) also provides a clue to accounting for the different temperature dependence of the oxygen permeability for the substituted and un-substituted samples.

By assuming the dependence of $\delta(1 - \frac{\delta}{2})$ on temperature also follows the Arrhenius law $\delta^0 \exp(-E_f/RT)$, the apparent activation energy for oxygen permeation E_a then consists of two terms, one being the energy barrier for oxygen migration E_m and the other being E_f associated with the term $\delta(1 - \frac{\delta}{2})$. For the un-substituted material, a negative value of -17 kJ/mol is calculated using the data given in Fig. 1, and ~ 44 kJ/mol for E_a , thus E_m is ~ 61 kJ/mol. For the Co-substituted material, E_f is 0.01 kJ/mol, thus the value of E_m is equal to E_a (~ 65 kJ/mol). It is interesting to note the substitution of Cu with Co does not result in a significant increase in the value of energy barrier for oxygen migration E_m .

5 Conclusions

The oxygen content δ in Co-substituted $\text{YBa}_2\text{Cu}_3\text{O}_{6+\delta}$ is significantly higher than that for the un-substituted one, and the value of δ in the former

does not change very much with changing temperature and oxygen partial pressure.

$\text{YBa}_2\text{Cu}_2\text{CoO}_{6+\delta}$ shows a much improved oxygen permeability in oxygen partial pressure gradient at the elevated temperature, which can be attributed to the desired distribution of oxygen ions and oxygen vacancy in the basal plane.

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