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Microstructural evolution and its influence on oxygen diffusion in yttrium-doped ceria thin films

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Abstract

Ceria doped with rare earth ions (Ce1−xMxO2−y (y = x/2)), which contain many oxygen vacancies, have become excellent electrolyte materials for solid oxide fuel cells and important buffer layers for coated conductors. In this paper, Y3+ ions were doped into the lattice of CeO2 to form Ce1−xYxO2−y (CYO) thin films regarded as buffer layers to reduce oxygen diffusion on silicon substrates. It was revealed that the CYO films gradually transformed from a complete fluorite structure into a defective fluorite structure with more and more oxygen vacancies as the proportion of Y3+ ions in CYO films increased from zero, and then the defective fluorite structure transformed into rare earth C-type structure when the proportion of Y3+ ions was beyond 0.5. Moreover, at the beginning, the degree of oxygen diffusion showed an uptrend; but after the proportion of Y3+ ions reached a certain value, the degree of oxygen diffusion turned into a downtrend.

1. Introduction

Ceria doped with rare earth ions (Ce1−xMxO2−y (y = x/2)) have more advantage for electrolyte materials of solid oxide fuel cells [1–4]. It is because the oxygen vacancy concentration increases continuously with the increase of the doping proportion of M3+ ions, which leads to a great improvement of their conductivity. Although ceria(CeO2) is a kind of oxygen ion conductor [3], the ionic conductivity of Ce1−xMxO2−y (CMO) increases gradually at first, and then decreases continuously after a certain doping proportion [5–8]. This is because, at the beginning, the doping proportion of M3+ ions is low, resulting in the disordered alignment of oxygen vacancies in ceria, which helps vacancy-ion exchange and enhances the ion conductivity. However, when the doping amount increases to a certain proportion, more and more oxygen vacancies start to align in an ordered manner, which is harmful to the vacancy-ion exchange and leads to the deteriorated conductivity. It is concerned with the transformation of the defective fluorite structure into the rare earth C-type structure caused by doping with rare earth ions. In fact, as shown in the previous paper, rare earth C-type structural oxides have very lower electrical conductivity than fluorite structural oxides [9].

Actually, the rare earth C-type structural oxide with ordered oxygen vacancies, like Y2O3 or Nd2O3, is a little similar to rare earth zirconate with pyrochlore structure, which can also be considered as an effective buffer layer material of coated conductors to reduce oxygen diffusion [10–12]. For example, La2Zr2O7 with pyrochlore structure has been one of the common superconducting buffer layer materials due to its ordered alignment of oxygen vacancies [12, 13]. However, there are few reports regarding to the influence of structure evolution of ceria doped with rare earth ions on oxygen diffusion when it is applied in a buffer layer. Another example is pyrochlore structural Y2(Zr1−xTi)xO7, which has been served as a buffer layer to reduce oxygen diffusion [14]. Both pyrochlore structural Y2(Zr1−xTi)xO7(YZTO) and rare earth C-type structural Ce1−xYxO2−y(CYO) have...
ordered structure, moreover, YZTO and CYO have something similar in their ability to reduce oxygen diffusion. Since the ionic radius of yttrium ($Y^{3+}$) is very close to that of cerium (Ce$^{4+}$), it is not easy to cause lattice distortion when $Y^{3+}$ ions are doped into the lattice of CeO$_2$, thus Ce$_{1-x}$Y$_x$O$_{2-y}$ ($y = x/2$) formed through substituting Ce$^{4+}$ ions by $Y^{3+}$ ions can be regarded as an infinite solid solution [5, 8]. Hence, in this work, the microstructural evolution of Ce$_{1-x}$Y$_x$O$_{2-y}$ (CYO) films prepared on silicon substrates and the specific influence of the ordered alignment of oxygen vacancies on oxygen diffusion at the interfaces between CYO films and silicon substrates are studied. These findings can provide a new selection basis for the development of buffer layer materials of coated conductors to reduce the harmful oxygen diffusion between NiW alloy substrate and YBa$_2$Cu$_3$O$_{7-\delta}$ superconducting layer.

2. Experimental

2.1. Preparation of Ce$_{1-x}$Y$_x$O$_{2-y}$ thin films

Due to high chemical homogeneity and relatively simple preparation process [15], in this investigation, sol-gel method was used to prepare Ce$_{1-x}$Y$_x$O$_{2-y}$ films. Yttrium nitrate hexahydrate ($Y(NO_3)_3 \cdot 6H_2O$ (AR)) and cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$ (AR)) were dissolved in 2-Methoxyethanol ($C_6H_{14}O_2$ (AR)) solvent using propionic acid ($C_3H_6O_2$) as cosolvent to synthesize eight bottles of Ce$_{1-x}$Y$_x$O$_{2-y}$ ($x = 0, 0.1, 0.3, 0.5, 0.6, 0.7, 0.8, 0.9$) precursor solutions with different proportions of the doping $Y^{3+}$ ions. The total cation concentration of each precursor solution was determined at around 0.3 mol/L. Then, CYO gel films were prepared on the silicon substrates by a dip-coating method at an appropriate pulling speed. The heat treatment process of CYO gel films is expressed in the following. All the gel films were transferred into a chamber electric furnace to carry on a given heat-treatment process (dwelled at 200 °C for 50 min and then at 500 °C for 30 min in air atmosphere) by which the gel films were transformed into CYO oxide films. A total of six layers of CYO films were fabricated layer after layer in this work. Thereinto, the first five layers were fabricated in accordance with the above procedures. The sixth-layer CYO gel films were kept at 200 °C for 50 min and then the furnace temperature was increased to 900 °C at a heating rate of 10 °C/min and kept at 900 °C for 60 min in air atmosphere, then decreased to the room temperature with furnace cooling. The same above procedures were conducted to fabricate all the eight CYO samples with various doping ratios of $Y^{3+}$ ions.

2.2. Characterization

X-ray diffractometer (XRD-7000 type) with Cu target was employed to identify the phases of CYO films with different $Y^{3+}$ doping proportions. The XRD measurement was carried out at the tube voltage of 30kV and tube current of 40mA with a scanning speed of 10°/min. Several representative films were selected to perform a cross-sectional observation on a JEM-3010 transmission electron microscopy (TEM). The cross-sectional TEM samples were prepared by a JIB-4000 focused ion beam (FIB) microscope. Finally, the lattice vibrations and lattice defects of all the CYO samples were analyzed by a HR800-type Raman spectrometer. The laser excitation wavelength was 325 nm with a Raman shift range from 200 cm$^{-1}$ to 1000 cm$^{-1}$ for CYO films; while the laser excitation wavelength was switched to 532 nm with the Raman shift ranging from 200 cm$^{-1}$ to 900 cm$^{-1}$ for SiO$_2$ interlayers.

3. Results and discussion

3.1. XRD analysis

Figure 1 (a) shows the diffraction peaks obtained by XRD patterns of CYO films. As shown in figure 1 (a), the four diffraction peaks come from the corresponding reflections of (111), (200), (220) and (311) lattice planes, which exactly belongs to the main diffraction lattice planes of CeO$_2$. While, the main diffraction lattice planes change into (222), (400), (440) and (622) for Ce$_{1-x}$Y$_x$O$_{2-y}$ ($x = 0, 0.1, 0.3$) when the doping proportion of $Y^{3+}$ ions is greater than 60%, and without any other diffraction peaks of impurities. This indicates that CYO films are pure phase and all the doping $Y^{3+}$ ions have been solutionized in the lattice of Ce$_{1-x}$Y$_x$O$_{2-y}$, i.e., the pure Ce$_{1-x}$Y$_x$O$_{2-y}$ solid solution is formed. It also suggests that the defective fluorite structure of Ce$_{1-x}$Y$_x$O$_{2-y}$ changes into other structure while $x$ is greater than 0.6. As shown in figure 1 (b), Ce$_{1-x}$Y$_x$O$_{2-y}$ ($x = 0, 0.1, 0.3$) have no characteristic diffraction peaks between the (200) diffraction peak around 33.5° and the (220) diffraction peak around 48.5°. When the doping proportion of $Y^{3+}$ ions exceeds 60%, several characteristic diffraction peaks of rare earth C-type structure appear at the range of 2 theta from 33.5° to 48.5° (shown in figure 1 (b)) [9]; as the doping proportion of $Y^{3+}$ ions continues to increase, the characteristic diffraction peaks of rare earth C-type structure in CYO become more and more obvious. By comparison with the PDF standard card, these C-type characteristic peaks coincide with the lines corresponding to the lattice planes on the PDF card. C-type characteristic peak of the (134) reflection plane appears at around 42.5° for Ce$_{0.5}$Y$_{0.5}$O$_{1.75}$.
Furthermore, the other four Ce$_{1-x}$Y$_x$O$_{2-y}$ (x = 0.6, 0.7, 0.8, 0.9) with the larger proportions of Y$^{3+}$ ions also show three C-type characteristic peaks coming from the reflection (411), (332) and (134) (or (431)) planes in the range of 2 Theta between 33.5° and 48.5°. Therefore, with the increase of the doping Y$^{3+}$ ions in Ce$_{1-x}$Y$_x$O$_{2-y}$, more and more rare earth C-type structures formed in Ce$_{1-x}$Y$_x$O$_{2-y}$ films. It is indicated that the transformation process from a defective fluorite structure into a rare earth C-type structure occurred while the doping ratio of Y$^{3+}$ ions was more than 50% [16].

3.2. TEM analysis
For CYO thin films with various doping proportions of Y$^{3+}$ ions, their ability to reduce oxygen diffusion at a high temperature of 900°C during heat treatment stage was explored by the cross-sectional TEM analyses of the selected six Ce$_{1-x}$Y$_x$O$_{2-y}$ (x = 0, 0.1, 0.3, 0.5, 0.7, 0.9) films samples made at a nearly same process. As indicated in figure 2 (a)–(f), all the six cross-sectional TEM images contain obvious three layers stacking from top to bottom, wherein, the bottom layers are single silicon substrates, the middle layers are silicon dioxide caused by oxygen diffusion and the top layers are CYO thin films with various doping proportions of Y$^{3+}$ ions. The thicknesses of CYO thin films were identified to be nearly the same grade having quite small differences, namely, they are 183nm, 203 nm, 191 nm, 181nm, 179nm and 192nm, corresponding to the thicknesses of CYO thin films as x equal 0, 0.1, 0.3, 0.5, 0.7 and 0.9, respectively. While the corresponding thicknesses of the silica interlayer were also identified to be 23 nm, 25 nm, 30 nm, 19 nm, 15 nm and 8 nm, respectively. It can be known that the thickness of the silica interlayer increases firstly and then decreases continuously with the increasing of the doping proportion of Y$^{3+}$ ions. Therein, Ce$_{0.7}$Y$_{0.3}$O$_{1.85}$ sample has the thickest silica interlayer among all the Ce$_{1-x}$Y$_x$O$_{2-y}$ samples. In other word, the more the amount of the ordered rare earth C-type structures in CYO thin films is (like Ce$_{0.1}$Y$_{0.9}$O$_{1.55}$), the stronger the ability of CYO films to reduce oxygen diffusion is, i.e., the thinner the thickness of silica interlayer is.

![Figure 1. (a) XRD patterns for Ce$_{1-x}$Y$_x$O$_{2-y}$ thin films and (b) The partial enlargement of XRD patterns in (a) with the 2 theta range from 30° to 50°.](image-url)
3.3. Raman spectrum analysis

Laser Raman spectrometer was employed to determine the special defective crystal structure of CYO thin films. To obtain strong Raman signals separately coming from CYO films and SiO<sub>2</sub> interlayer, two different excitation wavelengths (325 nm and 532 nm) were selected to perform Raman measurement and the results are presented in figure 3. It can be seen from figure 3(a) that the peak of each curve centered at around 320 cm<sup>-1</sup> is attributed to the Raman vibration mode of the silicon substrate [17]. When the proportion of Y<sup>3+</sup> ions is relatively low (x = 0, 0.1), Ce<sub>1−x</sub>Y<sub>x</sub>O<sub>2−y</sub> films have obvious Raman peaks centered at around 465 cm<sup>-1</sup>. These peaks are typical F<sub>2g</sub> vibration peaks, i.e., the first-order symmetric stretching vibration of (Ce−O)₈ bonds, which represents the Raman characteristic peaks of cubic fluorite structure of Ce<sub>1−x</sub>Y<sub>x</sub>O<sub>2−y</sub> [11]. As illustrated in figure 3(a), as the proportion of Y<sup>3+</sup> ions increases, the intensity of Raman peak at around 465 cm<sup>-1</sup> decreases gradually. This is because the larger the proportion of Y<sup>3+</sup> ions in Ce<sub>1−x</sub>Y<sub>x</sub>O<sub>2−y</sub>, the greater the distortion degree of the original CeO<sub>2</sub> lattice is, resulting that the less apparent the feature of the cubic fluorite structure of CeO<sub>2</sub> is. The peak at 465 cm<sup>-1</sup> disappears basically when the ratio of Y<sup>3+</sup> ions is 0.3. Furthermore, Ce<sub>0.1</sub>Y<sub>0.9</sub>O<sub>1.55</sub> has a small Raman peak at 380 cm<sup>-1</sup>, which is the Raman characteristic peak of rare earth C-type structure [9, 18]. Since the Raman signal of thin films sample is much weaker than the bulk or powder sample, only Ce<sub>0.1</sub>Y<sub>0.9</sub>O<sub>1.55</sub> films with the largest proportion of Y<sup>3+</sup> ions appear a quite small Raman peak of rare earth C-type.

Figure 2. Cross-sectional TEM micrographs of Ce<sub>1−x</sub>Y<sub>x</sub>O<sub>2−y</sub> thin films prepared on silicon substrates: (a) CeO<sub>2</sub>, (b) Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>1.95</sub>, (c) Ce<sub>0.7</sub>Y<sub>0.3</sub>O<sub>1.85</sub>, (d) Ce<sub>0.5</sub>Y<sub>0.5</sub>O<sub>1.75</sub>, (e) Ce<sub>0.3</sub>Y<sub>0.7</sub>O<sub>1.65</sub>, (f) Ce<sub>0.1</sub>Y<sub>0.9</sub>O<sub>1.55</sub>.
Besides, the peaks of CeO$_2$ films near 600 cm$^{-1}$ belong to the Raman vibration mode of oxygen vacancies in CeO$_2$ lattice. The intensity of this peak is weak because of few oxygen-vacancy defects in undoped CeO$_2$ films. The Raman peaks of other Ce$_{1-x}$Y$_x$O$_{2-y}$ films near 550 cm$^{-1}$ and 600 cm$^{-1}$ can be recorded as D$_1$ and D$_2$, respectively. D$_1$ peaks represent the Raman vibration modes of YO$_x$ (6$\leq x <$ 8) complexes with oxygen vacancies in Ce$_{1-x}$Y$_x$O$_{2-y}$, while D$_2$ peaks represent the Raman vibration modes of YO$_8$ complexes without oxygen vacancies [11, 19]. In that case, the YO$_x$ complex can be considered as YO$_6$ when the pure Y$_2$O$_3$ phase is formed. As shown in figure 3(a), the intensity of D$_1$ peak increases continuously with the increase of the proportion of Y$^{3+}$ ions, which indicates that the amount of YO$_x$ complexes with oxygen vacancies in Ce$_{1-x}$Y$_x$O$_{2-y}$ increases gradually with the increase of the doping proportion of Y$^{3+}$ ions. The intensity increase of D$_1$ peak can also be explained that many small Y$_2$O$_3$-like droplets in CYO films are gradually connected to form a Y$_2$O$_3$ phase domain and the area of this phase is increasing gradually [8]. The intensity of D$_2$ peak decreases gradually while the proportion of Y$^{3+}$ ions increases, implying the decrease of the amount of YO$_8$ complexes with the increase of the proportion of Y$^{3+}$ ions. Note that the D$_1$ peak shifts gradually to the right side (the direction to high Raman shift) as a result of changes in cell parameters of Ce$_{1-x}$Y$_x$O$_{2-y}$ caused by substitution of Ce$^{4+}$ ions by more and more Y$^{3+}$ ions [19]. As the proportion of Y$^{3+}$ ions increases, the degree of ordered alignment of rare earth C-type structural oxide Y$_2$O$_3$ in Ce$_{1-x}$Y$_x$O$_{2-y}$ increases, resulting in the decrease and disappearance of YO$_8$ complexes [20]. Therefore, it can be deduced that the crystal structure of CYO thin films gradually evolved from a disordered fluorite structure into an ordered rare earth C-type structure as the proportion of Y$^{3+}$ ions in the lattice of Ce$_{1-x}$Y$_x$O$_{2-y}$ increased.

As shown in figure 3(b), the peaks centered at 463 cm$^{-1}$ belong to Raman vibration of SiO$_2$ interlayers. It can be learned from figure 3(b) that the relative intensity of Raman peak (at 463 nm$^{-1}$) of SiO$_2$ interlayers gradually becomes stronger at first and then becomes weaker and even disappeared with the increase of the doping ratio of

**Figure 3.** Raman spectra for Ce$_{1-x}$Y$_x$O$_{2-y}$ thin films measured with different excitation wavelengths of (a) 325 nm and (b) 532 nm.
Y\textsuperscript{3+} ions. It is noted that the intensity of Raman peak (at 463 nm) of SiO\textsubscript{2} in CeO\textsubscript{2} film sample should also contain the contribution from the Raman vibration (at 465 nm) of cubic fluorite structure of CeO\textsubscript{2} because these two Raman peaks are quite close on Raman shift. Since the intensity of Raman peaks of cubic fluorite structure decreases with the increase of the doping proportion of Y\textsuperscript{3+} ions (as shown in figure 3(a)), the actual intensity of Raman peak of SiO\textsubscript{2} interlayers in all the Ce\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{2-y} thin films should increase with the increase of the doping proportion of Y\textsuperscript{3+} ions and reach the maximum when the doping ratio of Y\textsuperscript{3+} ions is up to 0.3. It indicates that the content of SiO\textsubscript{2} in Ce\textsubscript{0.7}Y\textsubscript{0.3}O\textsubscript{1.95} sample is more than those of any other Ce\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{2-y} samples, which coincides well with the changing tendency of the thickness of SiO\textsubscript{2} interlayer in TEM results presented in figure 2.

3.4. Discussion

The above oxygen diffusion results and law can be well elucidated by the diffusion theory based on vacancy exchange, and this theory is described in the following. At first, it should be pointed out that the general formula for the structure of rare earth C-type oxide is A\textsubscript{2}O\textsubscript{3}, which is a kind of cubic structure of rare earth oxide. The rare earth C-type structure can be considered as one kind of defective fluorite structure with orderly alignment of oxygen vacancies, and its lattice constant is two times as much as that of the corresponding defective fluorite structure. There are two oxygen vacancies in its one-eighth crystal cell, and the two oxygen vacancies align in an orderly manner at the whole crystal level \cite{18}. As shown in figure 4, if a foreign oxygen atom goes into the lattice of Ce\textsubscript{1-x}Y\textsubscript{x}O\textsubscript{2-y} films and attempts to occupy one of oxygen vacancies in the phase region of rare earth C-type structure (also regarded as Y\textsubscript{2}O\textsubscript{3}-like droplets), the oxygen vacancy will migrate to the O\textsuperscript{2-} position of Y\textsubscript{2}O\textsubscript{3} droplets and destroy the ordered structure existing in the CYO films \cite{18}. However, it is actually especially difficult to realize oxygen element diffusion through vacancy exchange in this rare earth C-type structure. The literature reported that oxygen diffusion coefficient of CYO increases firstly and reduces constantly after the doping proportion of Y\textsuperscript{3+} ions exceeds 15% at 1273K (1000 °C) \cite{1}. The variation tendency of the thickness of SiO\textsubscript{2} interlayer formed by oxidation and the variation tendency of the intensity of SiO\textsubscript{2} Raman peak (presented in figure 2 and figure 3 respectively) just provide powerful evidences for the above results and law of oxygen diffusion. Thus, it is believed that oxygen diffusion degree firstly aggravates with the increase of the doping ratio of Y\textsuperscript{3+} ions because of more and more defective fluorite phases forming in CYO thin films, but weakens constantly after a certain ratio of Y\textsuperscript{3+} ions due to more and more rare earth C-type phases appearing in CYO thin films.

4. Conclusion

To sum up, it can be concluded that the crystal structure of CYO thin films began to evolve step by step from defective fluorite structure with disordered oxygen vacancies into rare earth C-type structure with higher ordered oxygen vacancies as the doping proportions of Y\textsuperscript{3+} ions were elevated. CYO thin films with the doping
proportion (x = 0.9) of Y^{3+} ions showed the most apparent structural characteristic of rare earth C-type oxides. TEM and Raman analyses presented that the more the amount of the rare earth C-type structures in CYO thin films is, the stronger the ability to reduce oxygen diffusion is, which has been proved by the thicknesses variation of the silicon dioxide interlayers and the intensity variation of their Raman peaks. The result was also well explained by a theory of oxygen vacancy exchange in face-centered cubic lattice. Consequently, CYO thin films with higher doping proportion of Y^{3+} ions can be applied as a prospective buffer layer to reduce oxygen diffusion between NiW alloy substrate and superconducting layer. Moreover, it can be speculated that some other Ce_1-xM_xO_2-x/2 doped with a higher proportion of rare earth M^{3+} ions have similar reducing oxygen diffusion effects and the same applications.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary materials).

Disclosure statement

No potential conflict of interest was reported by the authors.

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