On the nucleation and paracrystal interspacing of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$

Ming-Yen Li, Pouyan Shen*

Institute of Materials Science and Engineering, National Sun Yat-sen University, 80424 Kaohsiung, Taiwan, ROC

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Abstract

A paracrystalline array of defect clusters was shown to form in Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ spinel in the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composites while prepared by a sintering route at 1650°C in air. Analytical electron microscopic observations indicated the spinel precipitate and its paracrystal predominantly formed at the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ interface and the cleavages/dislocations of the Co_{1-x}O host. Defect chemistry consideration suggests the paracrystal is due to the assembly of charge- and volume-compensating defects of the 4:1 type with four octahedral vacant sites surrounding one Co^{3+} -filled tetrahedral interstitial site. The interspacing of such defect clusters is 4.9 times the lattice spacing of the average spinel structure of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$. This spacing between defect clusters is about 0.98 times that of our previously studied undoped $\text{Co}_{3-\delta}\text{O}_4$. There is much larger (3.4 times difference) paracrystalline spacing for Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ than its parent phase of Zr-doped Co_{1-x}O .

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1. Introduction

Cobalt oxides are of interest because of their potential application in many fields. They have been intensively studied with respect to their electrocatalytic properties as well as to their selectivity to oxidation reaction for sensors. Zr-doped cobalt oxides are very interesting and promising system not only as sensors but also as catalysts for oxygen evolution and reduction reaction. The zirconia/ Co_{1-x}O interface is of interest to the fabrication of composite material [1] and catalysis of cobalt oxide supported on zirconia, in particular the catalytic activity for dehydrogenation [2] and oxidation of propane and CO [3] for possible application as automobile exhaust emission catalyst.

In this work, the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composites prepared by sintering and then annealing in air were studied by analytical electron microscopy (AEM). We focused on the effects of Zr dopant and heterogeneous nucleation sites on defect clustering to form paracrystal in the spinel-type lattice of $\text{Co}_{3-\delta}\text{O}_4$.

The paracrystalline distribution is such that the spacing between defects remains fairly constant but the relative lateral translation may occur more variably [4,5]. Fe_{1-x}O

having a considerable degree of nonstoichiometry ($x \leq 0.15$ [6] was known to possess defect clusters of 4:1 type with four octahedral vacant sites surrounding one Fe^{3+} -filled tetrahedral interstitial site [7]. When aged at high temperatures, the 4:1 clusters may assemble into larger units (e.g. 13:4, 16:5 and form a paracrystal [4,5]), which order further into Fe_3O_4 spinel or other ordered phases: p'' and p''' [8,9].

Co_{1-x}O with a much smaller x (ca. 0.01 [10]) than Fe_{1-x}O also formed spinel-type lattice of $\text{Co}_{3-\delta}\text{O}_4$, which is surprisingly with paracrystalline distribution of defect clusters while prepared by oxidizing/sintering Co_{1-x}O in air [11]. ($\text{Co}_{3-\delta}\text{O}_4$ is a normal type spinel according to magnetic measurements [12] and can be formed by spontaneous oxidation of Co_{1-x}O upon cooling below 900°C [13].)

In the present study, the sintered and annealed $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composites were studied with emphasis on the following points. First, to study whether a Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ paracrystal occur and whether it has interspacing of defect clusters different from that of undoped $\text{Co}_{3-\delta}\text{O}_4$. Second, to show that paracrystal development in Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ is affected by heterogeneous nucleation sites such as the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ interface and the cleavages/dislocations of the Co_{1-x}O host. Such knowledge may help the fabrication of $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composite materials [1] and the catalytic applications of cobalt oxide supported on zirconia at high temperatures [2,3].

* Corresponding author. Tel.: +886-7-5252000x4060; fax: +886-7-5254099.

E-mail address: pshen@mail.nsysu.edu.tw (P. Shen).

2. Experimental

ZrO₂ (Cerac, 2 μ m in size) and Co_{1-x}O (Cerac, 325 mesh) powders in 1:99 molar ratio (denoted as C₉₉Z₁) were ball milled in alcohol, oven dried at 100 °C, and then dry pressed at 650 MPa to form pellets ca. 5 mm in diameter and 2 mm in thickness. The pellets of C₉₉Z₁ were then sintered at 1650 °C for 24 h or 100 h in an open-air furnace and then cooled in the furnace.

X-ray diffraction (XRD, Cu K α , 40 kV, 20 mA, at 0.05° and 3 or 6 s per step up to 2 θ angle 110°) was used to identify the phases of the fired specimens. Scanning electron microscopy (SEM, JSM-6400, 20 kV) was used to study chemically etched (HCl + HF solution at room temperature for 10 min) surface for the distribution of ZrO₂ particles in the composites. Thin sections of the samples were Ar-ion milled to electron transparency and studied by AEM (JEOL 3010) at 300 kV for bright field image, dark field image, lattice image, selected area electron diffraction (SAED) pattern, and point-count energy dispersive X-ray (EDX) analysis. The EDX analysis was performed using L shell counts for Zr and K shell counts for Co and O, and the principle of ratio method without absorption correction [14]. The error was estimated to be within $\pm 5\%$. The electron diffraction pattern of the tetragonal (t-) and monoclinic (m-) phase of ZrO₂ was indexed according to the distorted version of c-fluorite cell as adopted previously [15].

3. Results

3.1. SEM and XRD

SEM observations indicated all the fired composites contain inter- and intragranular ZrO₂ particles in a matrix of Co_{1-x}O grains (Fig. 1) with considerable mutual solid solubility. The Co_{3- δ} O₄ precipitates predominantly occurred around the ZrO₂ particles and at the partially healed cleavages of the Co_{1-x}O grains. In fact, the healing of both inter- and intragranular cleavages involved the co-precipitation of Co_{3- δ} O₄ and secondary ZrO₂, similar to the case of cleaving-healing of the yttria-partially stabilized zirconia (Y-PSZ)/Co_{1-x}O composite upon cooling [16].

XRD indicated the fired composites contain predominant m-ZrO₂ and Co_{1-x}O with a minor amount of Co_{3- δ} O₄ spinel (Fig. 2). Least-squares fit of the *d*-spacings indicated the Co_{1-x}O has a constant lattice parameter of 0.4266 nm regardless of firing time at 1650 °C. This lattice parameter is larger than undoped Co_{1-x}O (0.4260 nm, JCPDS#09-0402) indicating a considerable dissolution of Zr in Co_{1-x}O. The Co_{3- δ} O₄ derived from Co_{1-x}O by oxidation was too scarce to give adequate XRD peaks for precise lattice parameter determination. Still, a slightly larger *d*-spacing of Co_{3- δ} O₄ indicated that there is a slight dissolution of Zr, in accord with the AEM-EDX result.

Fig. 1. SEM image (back-scattered electron image) of a representative C₉₉Z₁ composite prepared by sintering at 1650 °C for 100 h and then etched by HCl + HF solution. Note inter- and intragranular ZrO₂ particles (bright) in Co_{1-x}O matrix with Co_{3- δ} O₄ spinel (hardly visible at this scale) precipitated along grain boundaries and healed cleavages (see text).

Fig. 2. XRD traces for composites fired at 1650 °C for specified time periods and then cooled in the furnace: (a) and (b) C₉₉Z₁ samples fired for 24 and 100 h, respectively. Note rock-salt structured Co_{1-x}O peaks (denoted as C), spinel peaks (denoted as S) and m-zirconia peaks (denoted as m).

3.2. AEM

3.2.1. Zr-doped Co_{1-x}O

$\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composites fired at 1650°C for 24 h or 100 h always contain paracrystalline state of defect clusters in the Co_{1-x}O grain (Fig. 3). In general, paracrystal can be observed near the cleavages or rim of the Co_{1-x}O grain regardless of firing time at 1650°C . The satellite diffraction spots of Zr-doped Co_{1-x}O have a spacing ca. 1/2.9 times the lattice parameter in the reciprocal lattice (Fig. 3c). Thus, the paracrystalline distribution of defects is nearly 2.9 times the lattice spacing of the average structure of Zr-doped Co_{1-x}O . Point-count EDX analysis in the region containing paracrystals indicated that Zr content in Co_{1-x}O is less than 0.5 at.% (Fig. 3d). On the other hand, the Co content in ZrO_2 is much higher (ca. 6.0 at.%) according to EDX analysis of inter- or intragranular particles (not shown).

3.2.2. Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ spinel

AEM observations indicated that the $\text{Co}_{3-\delta}\text{O}_4$ spinel not only occurred at the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ interface (or Co_{1-x}O

grain boundaries) but also formed slabs along the $\{110\}$ or $\{100\}$ cleavages of the matrix Co_{1-x}O grains. These $\text{Co}_{3-\delta}\text{O}_4$ precipitates were analyzed by electron diffraction and dark field image to possess paracrystals. For the typical $\text{Co}_{3-\delta}\text{O}_4$ slab, its paracrystals tended to nucleate at the $\text{Co}_{1-x}\text{O}/\text{Co}_{3-\delta}\text{O}_4$ spinel interface as indicated by the image viewed in the zone axes of $[011]$ and $[\bar{1}11]$ in Figs. 4 and 5, respectively. The $\text{Co}_{3-\delta}\text{O}_4$ spinel always follows parallel crystallographic relationship with the Co_{1-x}O host. Still, Moiré fringes due to superimposed epitaxial phases can be avoided by tilting the $\{110\}$ spinel slabs into edge-on orientation such as in the $[\bar{1}11]$ zone axis (Fig. 5a). The paracrystal d -spacing of $\text{Co}_{3-\delta}\text{O}_4$ can thus be determined unambiguously to be 9.8 times the spinel 022 d -spacing (2.9 nm) either based on real-space image (Fig. 5a) or side-band diffraction spots (Fig. 5b). This paracrystalline spacing is about 4.9 times that of the average spinel cell dimension. Point-count EDX analysis indicated that Zr dissolution in the spinel particles (Fig. 5c) is not much different from Co_{1-x}O host (Fig. 3d).

Fig. 3. TEM (a) bright field image of Zr-doped Co_{1-x}O paracrystal (denoted as P) near the intragranular cleavage of Zr-doped Co_{1-x}O host (denoted as C), (b) dark field image taken with side band spots associated with $1\bar{1}1$ of Co_{1-x}O , (c) corresponding SAED pattern in $[011]$ zone axis showing fundamental and satellite spots of the paracrystalline lattice with a real space spacing ca. 2.9 times the lattice parameter of Zr-doped Co_{1-x}O , and (d) point-count EDX spectrum of the paracrystal showing Zr counts are rather limited. $\text{Co}_{99}\text{Zr}_1$ sample fired at 1650°C for 24 h.

Fig. 4. TEM (a) bright field image of a representative spinel slab precipitated parallel epitaxially at (110) cleavage of Co_{1-x}O . (b) Dark field image taken with side band spots associated with $\bar{1}\bar{1}1$ of spinel, (c) SAED pattern ($Z = [0\ 1\ 1]$) showing side-band spots of spinel paracrystal. $\text{Co}_{99}\text{Zr}_1$ sample fired at 1650°C for 100 h.

Fig. 5. TEM (a) dark field image ($g = 220$ of spinel) of spinel slab at a healed Co_{1-x}O (110) cleavage edge-on, (b) bright field image with inset electron diffraction pattern in $[\bar{1}\bar{1}1]$ zone axis showing paracrystal (220) spacing of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ spinel, (c) point-count EDX spectrum of the spinel paracrystal with rather limited Zr counts. The same specimen as Fig. 4.

Fig. 6. TEM bright field image with inset SAED pattern ([0 1 1] zone axis) of Zr-doped Co_{1-x}O showing parallel-epitaxial spinel precipitates (denoted as S) nucleated preferentially at dislocations with a line vector of [100] or [0 1 1]. The same specimen as Fig. 4.

Cooling below ca. 900 °C in air has also caused oxidation/precipitation of Zr-doped Co_{1-x}O to form Zr-doped $\text{Co}_{3-8}\text{O}_4$ at dislocations with $\langle 001 \rangle$ and $\langle 011 \rangle$ line vectors (Fig. 6). These spinel precipitates were probably nucleated at the same time, such as with specific undercooling below ca. 900 °C, in order to be of nearly the same size. Lattice image in Fig. 7 shows the parallel-epitaxial spinel domains have their $\{111\}$ and $\{200\}$ lattice planes quite coherently shared with the matrix Co_{1-x}O grain. However, dislocations and defect clusters at $\{100\}$ and $\{111\}$ steps were also observed (Fig. 7). The $\{111\}$ and $\{100\}$ faceted pores were also observed in the spinel precipitates (Fig. 8). These pores were likely formed by vacancy clustering in the Zr-doped $\text{Co}_{3-8}\text{O}_4$ at high temperatures, although Kirkendall and/or sintering relic pores cannot be excluded.

4. Discussion

4.1. Defect chemistry

Temperature dependence of $p\text{O}_2$ in atmosphere accounts for the oxidation of bulk and undoped Co_{1-x}O to form $\text{Co}_{3-8}\text{O}_4$ spinel below 900 °C [13]. Cobalt vacancies (V_{Co}''), interstitials ($\text{Co}_i^{\bullet\bullet\bullet}$), and 4:1 clusters ($[\text{Co}_i^{\bullet\bullet\bullet} + 4V_{\text{Co}}'' + 4\text{Co}_{\text{Co}}^{\bullet}]$) in undoped Co_{1-x}O were suggested to develop into paracrystal and then $\text{Co}_{3-8}\text{O}_4$ spinel also with paracrystalline distribution of defect clusters [11]. Besides oxidation upon cooling, Zr dopant is suggested to play an important role on defect clustering and paracrystal formation in the Co_{1-x}O and $\text{Co}_{3-8}\text{O}_4$ crystals as addressed in turn.

4.1.1. Zr-doped Co_{1-x}O

In m- ZrO_2 that co-exists with Co_{1-x}O and/or $\text{Co}_{3-8}\text{O}_4$, Zr^{4+} prefers to have seven-fold coordination as inferred from analogue zirconia [17]. Thus it is conceivable that Zr^{4+} reside in octahedral substitutional sites, instead of interstitial tetrahedral sites for the Co_{1-x}O lattice. The Zr^{4+} dopant is expected to cause charge-compensating defect clusters $[\text{V}_{\text{Co}}'' + \text{Co}_{\text{Co}}^{\bullet}]$ through the following equation in Kröger-Vink notation [18]:

Here $\text{Zr}_{\text{Co}}^{\bullet\bullet}$ signifies a dominating double positively charged zirconium at cobalt sites in the crystal lattice. It is also possible that the volume-compensating effect due to the substitution of Co^{2+} (effective ionic radii 0.065 nm for low spin) with Zr^{4+} (0.072 nm) in coordination number (CN) six [19] forced $\text{Co}_{\text{Co}}^{\bullet 3+}$ to enter the interstitial tetrahedral site, i.e. $\text{Co}_i^{\bullet\bullet\bullet}$, and, hence, more charge-compensating cation vacancies through the following equation (dominant $\text{Zr}_{\text{Co}}^{\bullet\bullet}$ as a representative):

The resultant 4:1 type defect clusters can then be activated to form paracrystalline ordered state and then spinel above 900 °C, i.e. the upper temperature limit for undoped Co_{1-x}O to form $\text{Co}_{3-8}\text{O}_4$ in atmosphere [13].

Oxygen vacancies can also be introduced around $\text{Zr}_{\text{Co}}^{\bullet\bullet}$ for volume compensation, and therefore affect the defect structure and the migration mechanisms across the $\text{Co}_{1-x}\text{O}/\text{ZrO}_2$ diffusion couples as experimentally proved for oxidized CoO–zirconia (CaO stabilized) eutectic [20] and Co_{1-x}O coating on zirconia (CaO stabilized) [21]. The abrupt change of oxygen concentration thus may account for the formation of $\text{Co}_{3-8}\text{O}_4$ at the $\text{Co}_{1-x}\text{O}/\text{ZrO}_2$ interface.

4.1.2. Zr-doped $\text{Co}_{3-8}\text{O}_4$

The defect structure of normal $\text{Co}_{3-8}\text{O}_4$, which can be described by the formula $(\text{Co}^{2+}_{\text{tet}})_8(\text{Co}^{3+}_{\text{oct}})_{16}(\text{V}_{\text{oct}})_{16}(\text{O}^{2-})_{32}$, is not well known but cation vacancies seem to be predominant lattice defects in this structure [22]. The paracrystal of undoped $\text{Co}_{3-8}\text{O}_4$ may be assembled from cobalt vacancies and cobalt interstitials via defect equations analogous to the case of parent Co_{1-x}O [11]. The extra Co^{3+} deviating from stoichiometric spinel, as denoted by δ in the formula $\text{Co}_{3-8}\text{O}_4$, may occupy both tetrahedral A sites and octahedral B sites at high temperatures as the case of so-called disordered spinel above 1150 K [23]. As for Zr-doped $\text{Co}_{3-8}\text{O}_4$, its δ value is raised by Zr-dopant (see Section 4.3.). The extra cobalt vacancies and Co^{3+} interstitials in Zr-doped $\text{Co}_{3-8}\text{O}_4$ may form extra 4:1 defect clusters analogous to Eqs. (1) and (2) for parental Zr-doped Co_{1-x}O . In the framework of alternating Co^{2+}O_4 tetrahedra and $\text{Co}^{3+}_4\text{O}_4$ cubes, which

Fig. 7. Lattice image of $\text{Co}_{3-\delta}\text{O}_4$ spinel precipitates in Co_{1-x}O host with a well-developed (100) and (111) interface (denoted by dashed line). Note nano-meter size defect clusters or disordered regions at (100) and (111) steps and more regular domains of the spinel lattice with dislocations denoted by T. The same specimen as Fig. 4.

build up into a face centered cubic lattice of 32 oxygen ions (Appendix A) [22], these extra 4:1 defect clusters may more or less link to affect the paracrystal spacing for $\text{Co}_{3-\delta}\text{O}_4$. It should be noted that co-flux of cation/oxygen vacancies would circumvent space charge during Kirkendall-pore formation for an ionic crystals [24]. Thus, oxygen vacancies, as a result of volume compensation for $\text{Zr}_{\text{Co}}^{\bullet\bullet}$ as mentioned, are expected to co-exist with cation vacancies in order to form pores within the $\text{Co}_{3-\delta}\text{O}_4$ crystal.

4.2. Heterogeneous nucleation of Zr-doped paracrystals

Paracrystal is expected to nucleate at free surface and dislocations where intrinsic/extrinsic defects segregate and short-circuit diffusion prevails. The work function measurements of the cleaved Co_{1-x}O single crystal indeed showed that intrinsic defects preferred to occur at free surface and therefore the Co_3O_4 structure formed within the near-surface layer under T - $p\text{O}_2$ conditions, which correspond to the stability of the CoO phase in the bulk [22]. It is an open question whether the phase diagram dealing with near-surface or near-interface consecutive regimes of forming cobalt

vacancies and then cobalt interstitials from Co_{1-x}O (Appendix B) can be extended to the case of generating such defects from $\text{Co}_{3-\delta}\text{O}_4$, either undoped [11] or Zr-doped. If near-surface or near-interface consecutive regimes are indeed effective for Zr-doped $\text{Co}_{3-\delta}\text{O}_4$, then the paracrystals are expected to form above 900°C , the equilibrium $\text{Co}_{1-x}\text{O}/\text{Co}_{3-\delta}\text{O}_4$ phase boundary for the bulk in air [13].

Dislocations, generated by sintering/coalescence process as demonstrated by the assembly of nanocrystalline titania [25] and CeO_2 [26], may also act as nucleation sites of the paracrystal. The space charge at these sites, as expected for rock salt-type ionic crystals [27], may favor clustering of charged species into the 4:1 and then paracrystalline ordered state.

Additional factor of capillary force at crack tip is of concern to the formation of paracrystals in spinel slabs, which healed Co_{1-x}O cleavages. Thermal-mismatch and zirconia-transformation induced cleaving of matrix phase upon rapid cooling was experimentally proved for Co_{1-x}O embedded with yttria-partially stabilized zirconia [16] and undoped ZrO_2 particles (to be reported elsewhere), respectively. Spontaneous healing during cooling was rationalized

Fig. 8. TEM (a) bright field image with inset SAED pattern ($Z = [011]$) showing parallel-epitaxial spinel precipitates in coalescence; (b) a further magnified view from area denoted by arrow showing $\{100\}$ and $\{111\}$ faceted pores. The same sample as Fig. 3.

by oxidation and exsolution processes besides self-healing, i.e. crack regression and/or pinching under the influence of capillary force [16]. A beneficial lower nucleation barrier at cleavage front and a higher growth rate in the cleavage healing direction may cause precipitation of paracrystals. The factor of growth kinetics accounts for the paracrystal formation on the two sides of the spinel slab that precipitates at the healing cleavage.

4.3. Spacing between defect clusters

The interspacing of defect clusters is 4.9 times the lattice spacing of the average spinel structure of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$. This spacing between defect clusters is about 0.98 times that of our previously studied case of undoped $\text{Co}_{3-\delta}\text{O}_4$ [11]. In other words, there is about 0.94 (i.e. $0.98 \times 0.98 \times 0.98$)

times difference in defect-cluster concentration. The δ value of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ is thus ca. 1.1 (i.e. $1/0.94$) times higher than undoped $\text{Co}_{3-\delta}\text{O}_4$.

The paracrystalline distribution of defect clusters is 2.9 times the lattice parameter of Zr-doped Co_{1-x}O , whereas 4.9 times the lattice spacing of the average spinel structure of Zr-doped $\text{Co}_{3-\delta}\text{O}_4$, i.e. nearly 9.8 times the lattice spacing of the parent rock-salt structure. A much larger ($9.8/2.9 = 3.4$ times difference) paracrystalline spacing for Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ than its parent phase of Zr-doped Co_{1-x}O can be rationalized by a lower extent of nonstoichiometry δ in the former if defect clusters are of the same type in the two lattices and the effect of defect clustering on electronic configuration and interionic distance is negligibly low [28]. If this is indeed the case, then there is about 40 (i.e. $3.4 \times 3.4 \times 3.4$) times difference in defect-cluster concentration. The paracrystals in the Co_{1-x}O and $\text{Co}_{3-\delta}\text{O}_4$ crystals when tailored by aliovalent dopants, such as Zr^{4+} in this study, are expected to affect catalytically active surface/bulk of cobalt oxide catalysts and may have potential applications as step-wise sensor of oxygen partial pressure at high temperatures.

5. Conclusions

1. Paracrystalline ordered state occurred in Zr-doped Co_{1-x}O and Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ spinel according to analytical electron microscopic study of the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ composites sintered at 1650°C in air.
2. The paracrystals predominantly nucleated at the $\text{ZrO}_2/\text{Co}_{1-x}\text{O}$ interface and at the cleavages/dislocations of the matrix Co_{1-x}O grains.
3. The Zr-dopant introduced extra cobalt vacancies and Co^{3+} interstitials for $\text{Co}_{3-\delta}\text{O}_4$ to form a smaller interspacing of paracrystal, i.e. 4.9 instead of 5.0 times that of average spinel lattice parameter. In addition, Zr-dopant may co-introduce cation and oxygen vacancies to form pores within the $\text{Co}_{3-\delta}\text{O}_4$ crystal.
4. There is much larger (3.4 times difference) paracrystalline spacing for Zr-doped $\text{Co}_{3-\delta}\text{O}_4$ than its parent phase of Zr-doped Co_{1-x}O .

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Appendix A. The unit cell of Co_3O_4

The structure consists of alternating Co^{2+}O_4 tetrahedra (A) and $\text{Co}^{3+}_4\text{O}_4$ cubes (B) build up into a face centered cubic lattice of 32 oxygens, after ref. [22].

Appendix B. The near-surface CoO/Co₃O₄ phase diagram

The phase diagram for the near-surface region results from the work function measurements of the cleaved CoO single crystal [22]. Regions 1, 2 and 3 denote consecutive regimes of forming cobalt vacancies, cobalt interstitials and then Co₃O₄ overlayer in oxidation runs. The bulk phase boundaries between regions 3 and 4 are based on thermodynamic calculation (equilibrium) and experimental data (transition line) of ref. [22].

References

- [1] J.I. Echigoya, S. Hayashi, J. Crystal Growth 129 (1993) 699–705.
- [2] L.A. Boot, M.H.J.V. Kerkhoffs, B.T. van der Linden, A.J. van Dillen, J.W. Geus, F.R. van Buren, Appl. Catal. A: General 137 (1996) 69–86.
- [3] G. Koyano, H. Watanabe, T. Okuhara, M. Misono, J. Chem. Soc. Faraday Trans. 92 (1996) 3425–3430.
- [4] T.R. Welberry, A.G. Christy, J. Solid State Chem. 117 (1995) 398–406.
- [5] T.R. Welberry, A.G. Christy, Phys. Chem. Miner. 24 (1997) 24–38.
- [6] B.E.F. Fender, F.D. Riley, in: L. Eyring, M. O'Keefe (Eds.), The Chemistry of Extended Defects in Non-Metallic Solids, North-Holland, Amsterdam, 1970.
- [7] C.R.A. Catlow, B.E.F. Fender, J. Phys. C: Solid State Phys. 8 (1975) 3267–3279.
- [8] P. Vallet, P. Raccach, Mem. Sci. Rev. Metall. 62 (1965) 1–29.
- [9] B. Andersson, J.O. Sletnes, Acta Crystallogr. Sect. A 33 (1977) 268–276.
- [10] S.M. Tomlinson, C.R.A. Catlow, J.H. Harding, J. Phys. Chem. Solids 51 (1990) 477–506.
- [11] W.H. Lee, P. Shen, J. Solid State Chem. 177 (2004) 101–108.
- [12] P. Cossee, Rec. Trav. Chim. Pays-Bas 75 (1956) 1089–1096.
- [13] M. Oku, Y. Sato, Appl. Surf. Sci. 55 (1992) 37–41.
- [14] D.B. Williams, Practical Analytical Electron Microscopy in Materials Science, Philips Electronic Instruments, Inc., Electron Optics Publishing Group, Mahwah, NJ, 1984, p. 157.
- [15] G. Teufer, Acta Crystal. 15 (1962) 1187–1188.
- [16] W.H. Lee, P. Shen, Mater. Sci. Eng. A 332 (2002) 262–269.
- [17] P. Li, I.W. Chen, I.E. Penner-Hahn, Phys. Rev. B 48 (1993) 10074–10081.
- [18] F.A. Kröger, H.J. Vink, Solid State Phys. 3 (1956) 307–435.
- [19] R.D. Shannon, Acta Crystal. Logr. Sect. A 32 (1976) 751–767.
- [20] J. Bentley, S. McKernan, C.B. Carter, A. Revcolevschi, in: Proceedings of the Inst. Phys. Conference Ser. No 138: Section 2, Electron Microscopy and Analysis, IOP Publishing, Bristol, UK, 1993, p. 39.
- [21] H.I. Yoo, J.H. Lee, J. Phys. Chem. Solids 57 (1996) 65–73.
- [22] J. Nowotny, W. Weppner, M. Sloma, in: J. Nowotny, W. Weppner (Eds.), Non-Stoichiometric Compounds Surfaces, Grain Boundaries and Structural Defects, Kluwer Academic Publishers, Dordrecht, 1989, pp. 265–277.
- [23] X. Liu, C.T. Prewitt, Phys. Chem. Mineral. 17 (1990) 168–172.
- [24] W.H. Lee, P. Shen, Micron 33 (2002) 555–559.
- [25] R.L. Penn, J.F. Banfield, Science 281 (1998) 969–971.
- [26] W.H. Lee, P. Shen, J. Crystal Growth 205 (1999) 169–176.
- [27] A. Atkinson, R.I. Taylor, Phil. Mag. A 43 (1981) 979–998.
- [28] W.L. Smith, A.D. Hobson, Acta Cryst. B 29 (1973) 362–363.