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Phases in $Ce_{0.5}Zr_{0.5}O_{2-x}$ system

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Abstract

Using high-resolution electron microscopy (HREM), techniques reveal new pyrochlore-type phase with composition $Ce_2Zr_2O_{7.5}$ and composition domains in $Ce_{0.5}Zr_{0.5}O_{2-x}$ system.

Keywords: $Ce_2Zr_2O_{7.5}$; OSC; Pyrochlore-type structure; Composition domain

1. Introduction

Ce–Zr–O system has attracted great attention in three-way catalyst for automobile exhaust gases [1,2]. Oxygen storage capacity (OSC) is the basis of three-way catalyst [3]. OSC of the oxides is result of the reversible variation of ratio Ce^{4+}/Ce^{3+} under reduction or oxidation condition. The reversible variation of ratio Ce^{4+}/Ce^{3+} is function of both temperature and oxygen partial pressure instead of only temperature.

Leonov et al. [4,5] indicated that if the Ce^{4+} cations are reduced to the Ce^{3+} state, the system ZrO_2–CeO_2 should transfer into the system ZrO_2–Ce_2O_3. However, these two systems have completely different phase diagrams as shown in Fig. 1. The influence of oxygen partial pressure on the phase relation of solid solutions in Ce–Zr–O system is that the Ce^{4+} in a solid solution of ZrO_2 will be reduced to Ce^{3+} at increased temperature in reducing atmospheres (such as H_2, CO and NH_4) or under a vacuum of 10^{-4} to 10^{-5} Torr, or in an inert atmosphere (such as Ar and He) or in the atmosphere of flame furnaces with low oxygen partial pressure (for example, oxygen partial pressure 0.01 Torr at 1400 °C). The system of ZrO_2–CeO_2 has three phase regions, such as monoclinic (m), tetragonal (t) and cubic (c) phases, but in the system of ZrO_2–Ce_2O_3 the cubic, $Ce_2Zr_2O_7$, oxide with a pyrochlore structure (p) is a stable phase in the composition range from 44 to 57 mol% Ce_2O_3. From 3 to 44 mol% of Ce_2O_3, the pyrochlore phase is equilibrium with m-type ZrO_2–Ce_2O_3 solid solution under 1000 °C and with a t-phase above this temperature. At room temperature, t-phase is not stable in ZrO_2–Ce_2O_3 system. In the 57–100 mol% of Ce_2O_3 region, there is a cubic phase region around 81–85 mol% of Ce_2O_3. From 57 to 81 mol% of Ce_2O_3, the pyrochlore phase is equilibrium with the cubic phase. Recent investigation of this system confirms Leonov's report. However, the result of Yashima et al. [6,7] provide detail information of the t- and c-type phases in CeO_2–ZrO_2 system under oxidation condition.

In CeO_2–ZrO_2 system, there are two phases: fluorite-type cubic and tetragonal phases (or distorted fluorite-type structure with $c/a > 1$ called as t′ and t″) under 1000 °C. The c/a value may vary with different ratio of Ce/Zr. The phase transition from c to t′ or c to t″ or t′ to t″ is diffusionlese and reversible above 400 °C in air. The c–t″ transition is accompanied by oxygen displacement in fluorite-type structure. The investigation of Otsuka-Yao-Matsuo and co-workers [8–10] reveals a new cubic phase, which they called as κ-phase, in the ZrO_2–Ce_2O_3 system. In Leonov's report, the oxide with composition of 50 mol% of Ce_2O_3 and 50 mol% of ZrO_2 has pyrochlore structure, but they did not mention what will happy while it is oxidized. The formation of κ-phase

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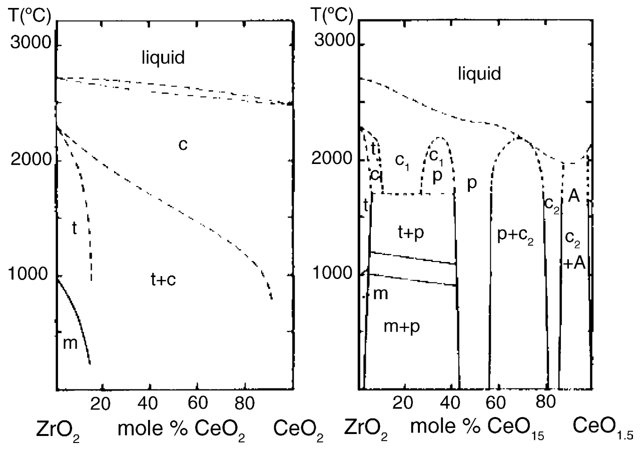

Fig. 1. Phase diagrams of (a) ZrO_2–CeO_2 [4] and (b) ZrO_2–Ce_2O_3 [5].

was that the sample heated up to 600–1300 °C for 10–18 h under reduced atmosphere, then cooled down to mediate temperature (for example, 600–400 °C) to oxidize it in oxygen atmosphere. This process is similar to the intercalation of oxygen into the pyrochlore oxide $Ce_2Zr_2O_7$ [11].

In this paper, we report our results of the $Ce_{0.5}Zr_{0.5}O_{2-x}$ oxide.

2. Experimental

Composition of the sample is $Ce_{0.5}Zr_{0.5}O_{2-x}$. It was prepared by soft chemistry route. Powder of the sample was heated up to 1100 °C for 2 h in 10% hydrogen flow and cooled down to 600 °C for 4 h in air, then cooled to room temperature. The sample was load on a holy carbon grid and observed in JEOL 4000 EX electron microscope.

3. Results and discussion

3.1. Pyrochlore structure

Pyrochlore structure was described as fluorite-related structure [12]. In fluorite structure, the cations form a face-centered-cubic array and the anions are located in the tetrahedral interstices of the cationic array. But there are two types of cations, A and B, and they are ordered in alternate $\pm\langle 1\,1\,0\rangle$ rows in every other $\{0\,0\,1\}$ plane as shown in Fig. 2. In the projection of pyrochlore structure along [1 1 0] direction, A and B atom rows can be clearly seen separately between two planes with equal A and B atoms. If A and B atoms do not order, then this character should be disappeared.

Using high-resolution electron microscopy (HREM) image may demonstrate where the oxygen vacancy and distortions are located. That means it may be possible to demonstrate the difference between the typical pyrochlore- and pyrochlore-type phase with disordered or partial disordered A and B atoms in a crystal. Pyrochlore-type phase means that the ordered oxygen vacancy forms a superstructure which similar to pyrochlore structure. But the content of oxygen vacancy may or may be not same as typical pyrochlore phase. Formula of this phase may be as $A_2B_2O_{7+\delta}$ $(0<\delta<1)$. Diffraction pattern of pyrochlore phase in [1 1 0] direction is shown in Fig. 2(f). The intensity of (0 0 2) is weaker than one of (1 −1 1) or (−1 1 1). But the intensities of (0 0 4), (2 −2 2) and (−2 2 2), which contributed by fluorite unit, are almost same. The weaker intensity of (0 0 2) indicates ordering of the A and B cations and the cubic unit cell of pyrochlore structure.

3.2. New phase

3.2.1. Electron diffraction data

Fig. 3(a) shows the experimental electron diffraction pattern of a new phase in [1 1 0] direction of fluorite structure. The feature of pyrochlore structure still may be seen in this diffraction pattern, but new set of extra-spots appear at the middle between 0 0 0 and 0 0 2 spots indexed as (0 0 1). That type of spots is the character of body-center-cubic type structure in [1 1 0] orientation. That implies the new phase is a body-center-cubic type structure with same dimension of pyrochlore phase.

The ordering degree of Ce and Zr cations may be indicated in the intensity difference between (1 −1 1), (−1 1 1) and (0 0 2) diffraction spots. It seems that the intensity difference existed, but is not definite. The new extra-spots are very weak in comparison with others. That may imply the oxygen vacancy ordered in a body-center-cubic fashion, but the Ce and Zr cations are ordered partially. If this is the case a model for this new phase may be given in Fig. 3(b). The detail discussion about modeling will be given in other paper [13].

An important point is that it is impossible to use the two types of fluorite unit constructing a body-center-cubic array of oxygen vacancies. That means the oxygen content in the new phase should be different from pyrochlore structure. Using two fluorite's unit with two oxygen vacancies and six fluorite units without any oxygen vacancy can build up a body-center-cubic array of oxygen vacancies with same dimension of pyrochlore unit cell. This structure still is fluorite-related and oxygen-deficient structure, but it has a composition as $Ce_2Zr_2O_{7.5}$. Based on Kang–Eyring principles of fluorite modules theory [14], this is possible and the orientation domains should exist. The oxygen vacancy array and the distortion of its neighbor atoms lead the weak intensities of the bcc-type diffraction spots.

In pyrochlore structure the Ce cation should be 3+ and Zr cation always is 4+. The sample was heated up under reduced atmosphere and oxidized at mediated temperature under air or oxygen. Ordering the cation need high temperature with keeping Ce being 3+, so it is necessary to have reduced atmosphere. Ordering cations should anneal the sample for long time. At 1100 °C, it is difficult to order

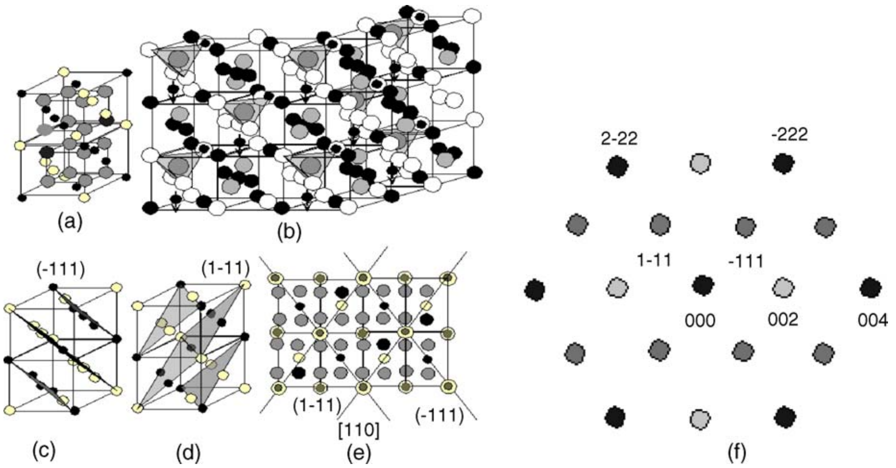

Fig. 2. Typical pyrochlore structure. (a) The basic unit of two types of fluorite unit, (b) the structure of pyrochlore phase, (c) outline of the −1 1 1 planes to demonstrate two different planes with different A and B atom numbers, (d) outline of 1 −1 1 planes to demonstrate equal number of A and B atoms, (e) [1 1 0] projection of the pyrochlore structure to demonstrate the difference between (−1 1 1), (1 −1 1) and (0 0 2) due to the different number of A and B atoms and (f) diffraction pattern of pyrochlore structure in [1 1 0] orientation. The intensity difference gives the indication of ordering of the A and B cations and the oxygen vacancies.

the cations. At 600 °C, the cerium cation may partially be oxidized and the mixture of Ce^{4+} and Ce^{3+} will exist and therefore Ce^{4+} may play as Zr^{4+} role for ordering of oxygen vacancies.

In the sample with same nominal composition and different treatments, there is other pyrochlore-type phase with fcc-type structure and same composition $Ce_2Zr_2O_{7.5}$ [15].

3.2.2. High resolution image of the new phase

The projection of fluorite structure in [1 1 0] direction may demonstrate the arrangement of Ce and Zr cations and oxygen vacancies of the new phase. Therefore HREM image may reveal the arrangement of the cationa and the oxygen vacancies. Fig. 4 is a HREM image of the new phase in [1 1 0] orientation of fluorite structure. The digit diffraction patterns (DDPs) are inserted. The DDP at low left corner was taken from left edge of the HREM image. It shows the (0 0 1)-type spots indicating a body-center-cubic structure. On the HREM image the fluorite sublattice can be seen at the very thin edge. As mentioned before, the mixed Ce and Zr atoms rows have different contrast from the Ce rows or Zr rows, which give sharp white dots. The sharp white dots have same as fluorite sublattice, but with double d spacing. The body-center-cubic unit cell may be seen carefully at the mixed Ce and Zr rows with slightly whiter. Similar situation may be seen at top right corner. However, at low right corner the DDP conspicuously shows the unit cell of the new phase, which is body-center-cubic structure.

Fig. 5 shows a HREM image in [0 0 1] direction. It also demonstrates the unit cell of the new phase. The inserted DDPs were taken from each of quarter part of the image. The

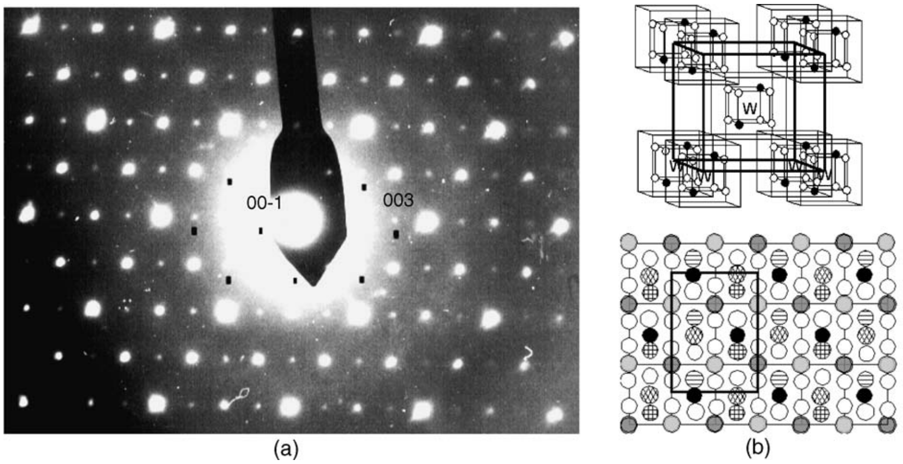

Fig. 3. (a) Experimental diffraction pattern of a new phase in $Ce_{0.5}Zr_{0.5}O_{2-x}$ oxide. The extra-spots ((0 0 1)-type spots) indicate the new phase is a body-center-cubic type structure. (b) Model of a body-center-cubic structure of the new phase and its projection on [1 1 0] orientation of fluorite structure.

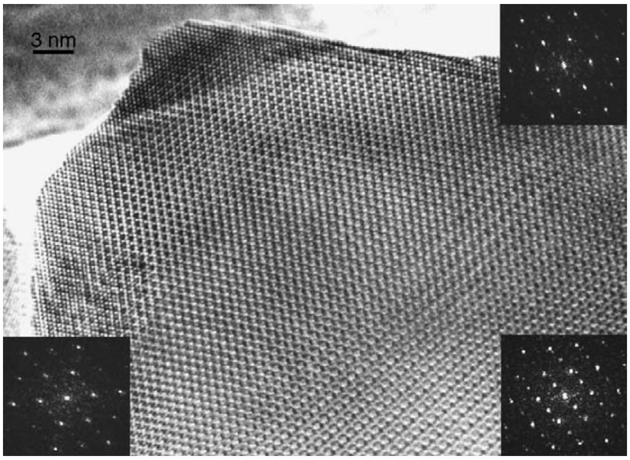

Fig. 4. A high-resolution electron microscopy (HREM) image of the new phase in [1 1 0] orientation of fluorite structure. At thin edge, each white dot is corresponding to a cation row. The digit diffraction patterns (DDPs) from different areas of the image are inserted. The body-center-cubic unit cell is clearly shown in each DDP inserted.

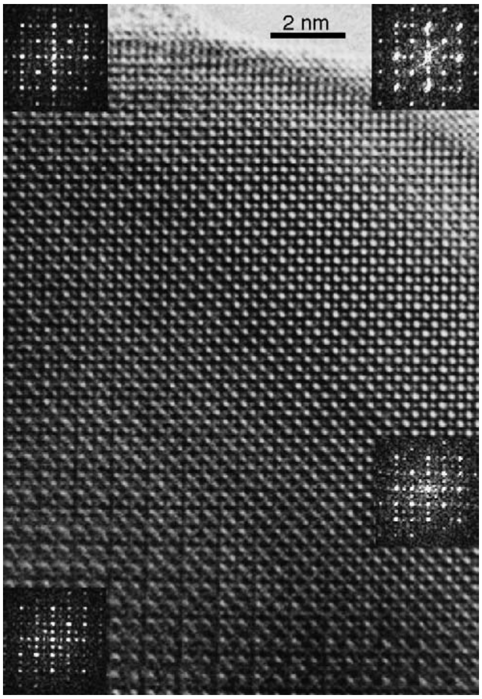

Fig. 5. HREM image of the new phase in [0 0 1] direction. The DDPs of each quarter region are inserted. Top right corner is a domain of pyrochlore phase.

digit diffraction patterns at top left, low left and low right part of the image are typical pattern of body-center-cubic structure, but the DDP at top right region is a diffraction pattern for pyrochlore structure in [0 0 1] orientation of fluorite. Therefore, a domain of pyrochlore phase existed in the crystal. The darker lines contrast in the image may come from the oxygen distortion due to oxygen vacancy.

Fig. 6(a) gives the comparison of pyrochlore structure and the model structure of the new phase with a bcc-type structure. The oxygen vacancies of model structure of the new phase located in ⟨1 1 0⟩ direction and they are separated by four (1 1 0) planes, but in pyrochlore structure it separated by two (1 1 0) planes. This is very useful to discriminate the bcc-type new phase. Fig. 6(b) shows the mixture of pyrochlore and the new phase. It is worth to notice that the modulation contrast can be seen around the new phase. The spacing between the modulations is almost same as the bcc phase in this orientation. This modulation may be directly related to the oxygen vacancy as same as the situation in the Ce, Pr and Tb higher oxides.

3.3. Relationship between fluorite-, tetragonal- and pyrochlore-type phases

As mentioned before, in Ce–Zr oxide system there are mainly three type phases, fluorite- (F), tetragonal- (t) and

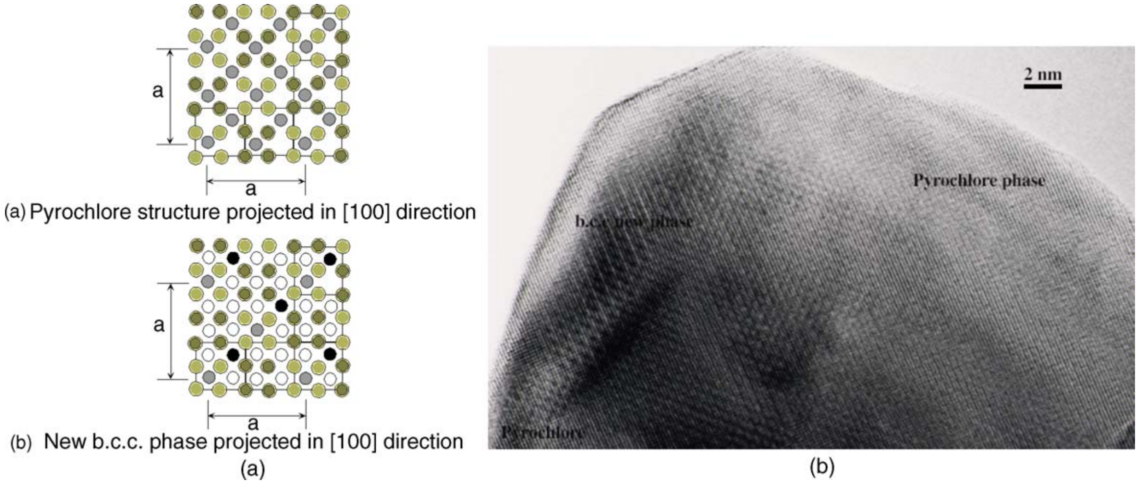

Fig. 6. (a) Comparison of the oxygen vacancy array in pyrochlore structure and the model of new phase with bcc structure. (b) The mixture of pyrochlore phase and the new phase with bcc structure. Modulation contrast can be seen around the new phase.

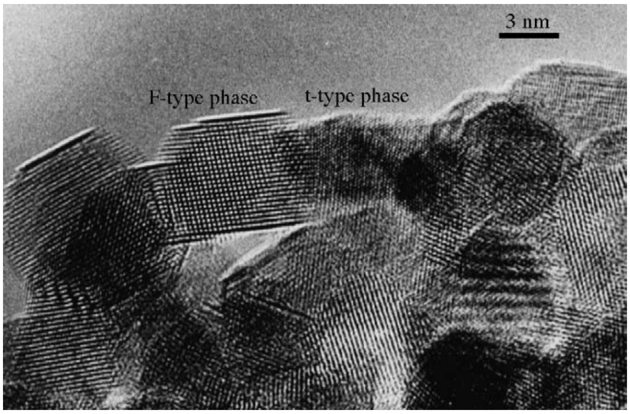

Fig. 7. Mixture of F- and t-type phases in $Ce_{0.5}Zr_{0.5}O_2$ oxide.

pyrochlore-type (p) phases. If the cerium content is more than about 80 mol% in the oxide at lower temperature it should be fluorite-type phase under oxidation environment, but under a reduced atmosphere it may have a mixture of pyrochlore- and pyrochlore-type phases. If the cerium content is 15–80 mol% there are always multiphase containing fluorite- and tetragonal-type phases. The t-type phases have different c/a value based on the content of zirconium, the thermal history and the preparation method. It is very hard, if it is not impossible, to prepare a solid solution with nominal composition. Fig. 7 shows the two solid solutions with different cerium content: one is F-type phase and other is t-type phase having c/a value ≈1.01. The t-type phase can be minimized by special preparation method, but never can be removed completely [16]. When these phases heated up to higher temperature, for example 1000 °C or more, they will sinter together. The multiphase feature makes the sintering process to be difficult that improves the thermal stability of CeO_2. If sintering is in a reduced atmosphere they can form pyrochlore-type phase with different cerium content. Homogeneity of the sintered sample depended on temperature and time. If the cerium content is higher, then pyrochlore-type phase may have more oxygen or less oxygen vacancy. Mixture of the domains with different oxygen content likely is the typical character of these oxides as shown in this paper. The F-, t- and pyrochlore-type phases have the ability to store oxygen. In other words, they have OSC.

4. Conclusion

Using HREM technology reveal the multiphase feature of $Ce_{0.5}Zr_{0.5}O_2$ oxide. Under oxidation condition there are F- and t-type phases. When it heated up to 1000 °C or more under reduce atmosphere and re-oxidized at mediate temperature, it is a mixture of domains of pyrochlore- and pyrochlore-type bcc phase. A structure model of a new phase with a bcc-type structure is proposed. The F-, t- and pyrochlore-type phases are responsible for the function of oxygen storage capacity of these oxides.

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