

Phase Relations at 1500°C in the Ternary System $\text{ZrO}_2\text{--Gd}_2\text{O}_3\text{--TiO}_2$

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Phase relations at 1500°C in the ternary system $\text{ZrO}_2\text{--Gd}_2\text{O}_3\text{--TiO}_2$ have been determined by the powder X-ray diffraction of samples prepared by standard solid state reaction. A large area of this ternary oxide system centered on the $\text{Gd}_2\text{Ti}_2\text{O}_7\text{--Gd}_2\text{Zr}_2\text{O}_7$ join was shown to exhibit the pyrochlore and defect fluorite structures. The pyrochlore structure was observed for stoichiometries as far from the ideal $M_4\text{O}_7$ as $M_4\text{O}_{6.7}$ and $M_4\text{O}_{7.4}$, although the degree of disorder seemed much higher at these stoichiometries. On further deviation from the ideal $M_4\text{O}_7$ stoichiometry a smooth transition to fluorite average structure was observed for Zr-rich compositions. None of the other binary phases were observed to show significant extent of solid solution into the ternary region. © 2001 Academic Press

INTRODUCTION

Solid oxide fuel cells are at the forefront of the search for more efficient and environmentally friendly means of energy conversion because of their potential in combined heat and power generation from either hydrocarbon fuels or hydrogen. Most current development centers on designs based on the yttria-stabilized zirconia (YSZ) electrolyte, with Ni/YSZ cermets as the preferred anode (1). In the cermet anode materials, the YSZ provides the oxide ion conduction and the nickel provides the electronic conduction. This means that the electrochemical oxidation of the fuel gas can only occur at the triple points between the oxide ion conductor, the electronic conductor, and the fuel gas. The Ni/YSZ cermet has several other disadvantages including carbon deposition at the anode (2), the low tolerance of nickel to sulfur (3), and the sintering of the nickel on prolonged operation (4).

Our objective has been to search for new candidate materials for SOFC anodes, and attention has been focused on the use of early transition metal oxides. Oxides have several advantages over metals, in that they are potentially less

likely to promote coking, i.e., carbon buildup, and less likely to suffer from sulfur poisoning. Also, the accessibility of mixed valence states facilitates electronic conductivity and generally enhances catalytic activity. Thus in a mixed conducting anode the electrochemical reaction can occur over the entire electrode/gas interface as opposed to the three point contacts between the electrode, electrolyte, and fuel gas (5).

In this study, we report the phase relations at 1500°C in the ternary system $\text{ZrO}_2\text{--Gd}_2\text{O}_3\text{--TiO}_2$; this temperature was chosen as it was the temperature used to synthesize these refractory oxides. Although 1000°C might have been a more interesting temperature from a technological perspective it is very difficult to attain thermodynamic equilibrium at this temperature. Previously the phase relations in this system have only been studied to a limited extent, particularly relating to the binary systems and the pseudo-binary join $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$. The search for potential anode materials in this system has primarily been focused on the “stoichiometric” pyrochlore compositions in the system $\text{Gd}_2\text{Zr}_{2-x}\text{Ti}_x\text{O}_7$, i.e., where the cation-to-oxygen ratio is 4:7 ($M_4\text{O}_7$). No report has previously been made on the extent of nonstoichiometry of the single-phase fluorite and pyrochlore regions in the ternary system. Oxide phase diagrams are typically reported as ratios of the oxides; however, in crystal chemical terms cation atomic ratios are more important. In this study, we predominantly consider atomic ratios, with some secondary discussion of molar ratios.

Background

The general formula of the oxide pyrochlores can be written as $A_2B_2O_6O'$ with four crystallographically nonequivalent kinds of atom. The space group of the ideal pyrochlore structure is $Fd\bar{3}m$ and there are eight formula units per cell ($z = 8$). The structure is composed of two types of cation coordination polyhedron. The A cations (usually $\sim 1 \text{ \AA}$ ionic radius) are eight coordinated and the smaller B cations ($\sim 0.6 \text{ \AA}$ ionic radius) are six-coordinated. Apart from the general rules regarding allowed (hkl) X-ray

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reflections for the $Fd3m$ space group, the additional rules arising from the special site occupancies for the pyrochlore structure are that h , k , and l must be equal to $4n + 2$ or $4n$, or that $h + k + l$ must be equal to $2n + 1$ or $4n$. Due to the symmetry of the sites, only one positional parameter, the 48f oxygen u value needs to be defined in the structure containing four different kinds of atoms, A , B , O , and O' . The u parameter for most pyrochlores generally has a value between 0.309 and 0.355.

The $(3+, 4+)$ pyrochlore phases such as those based on Gd^{3+} , Zr^{4+}/Ti^{4+} are large in number and the existence of Ln^{3+} ions with a systematic variation in ionic radius enables one to exactly define the stability field of $(3+, 4+)$ pyrochlores in terms of radius ratio. The relative ionic radii, $RR = (r_A^{3+}/r_B^{4+})$, and the oxygen parameter u govern the formation and stability of the oxide pyrochlore. Pyrochlores can form for $RR = 1.46$ to 1.80 (e.g., $r_{Gd}/r_{Zr} = 1.47$ and $r_{Gd}/r_{Ti} = 1.75$) at atmospheric pressure. The relatively large ionic radius of Zr^{4+} on the B site in $Gd_2Zr_2O_7$ results in a high value of the oxygen parameter, u , of about 0.375.

In describing this ternary system, the pyrochlore structure is best viewed in terms of the fluorite-type cell due to coexistence of these two phases. The fluorite structure, with space group $Fm3m$, consists of a cubic close-packed array of zirconium ions, with oxygen occupying all the tetrahedral sites. The pyrochlore structure can be considered as an anion deficient superstructure composed of eight defect fluorite blocks. The oxygen ions occupy the 48f and 8a sites and leave the 8b site systematically vacant. Thus $\frac{1}{8}$ of the anion sites in fluorite become empty interstitial sites in pyrochlore. This ordering on the anion and cation sublattices results in a unit cell edge twice that of the equivalent fluorite cell.

The phase relationships and properties of the $ZrO_2-Gd_2O_3-TiO_2$ system have been studied previously, especially for the binary systems. Phase diagram studies of the binary system $Gd_2O_3-ZrO_2$ have been performed by Perez y Jorba, Lefèvre, and Rouanet and Foex (6–8). Although there is disagreement on the phase relations reported by these authors, there are some consistencies. Perez y Jorba reported a tetragonal ZrO_2 solid solution, a cubic fluorite-pyrochlore-fluorite region, a hexagonal region, and a C-type region. Lefèvre reported the same ZrO_2 phase and cubic phase, but did not report on compositions greater than 33 at.% Gd^{3+} . Rouanet and Foex also reported the tetragonal ZrO_2 solid solution and the face-centered cubic region but the phase diagram cannot be directly compared to the two earlier diagrams as the temperature range studied by Rouanet and Foex was only above 1800°C. Bhat-tacharyya and Agrawal studied $ZrO_2-Gd_2O_3$ compositions containing up to 15 at.% Gd^{3+} , prepared by three different methods comparing their sinterability and extent of stabilization (9). It has been reported that only 5.8 at.% Gd^{3+} is needed for complete stabilization of the tetragonal phase

(10, 11), although this does not agree with Lefèvre (7). Single crystals were studied by Kang *et al.* (12). They reported the unit cell parameters of 18, 22, and 26 at.% Gd^{3+} as 5.164, 5.172, and 5.184 Å respectively and also reported peak broadening in Raman spectra caused by point defects such as anion vacancies and substituted cations. This type of peak broadening is typical of disordered phases and has been reported previously (13). The decrease in the Raman shift is due to the weakening of the bond strength of the nearest-neighbor Gd–O pair or the decrease of the nearest-neighbor oxygen atoms around a Gadolinium ion with increasing Gd_2O_3 content.

The binary system $Gd_2O_3-TiO_2$ has also received little attention in terms of phase relationship studies. Waring and Schneider reported the binary phase diagram in 1965 (14). A line phase and two solid solutions were reported. The line phase Gd_2TiO_5 exhibits two polymorphs with a transformation at 1712°C. One solid solution is based on $Gd_2Ti_2O_7$ pyrochlore and the other, which only exists above 1600°C, is based approximately on $Gd_6Ti_2O_{13}$. No other reports have been made since.

In the ternary system $ZrO_2-Gd_2O_3-TiO_2$ the existence of a solid solution between the stoichiometric binary pyrochlores $Gd_2Zr_2O_7$ and $Gd_2Ti_2O_7$ was reported by Moon and Tuller (15). The zirconate end member is highly disordered; i.e., Gd^{3+} and Zr^{4+} are similar in size and can thus occupy the same six- and eight-fold sites. The titanate end member is highly ordered because of the large difference in the ionic radii of the Gd^{3+} and the Ti^{4+} . The degree of order within the structure can thus be controlled by choice of composition and hence electronic and ionic conductivities can also be controlled. Moon and Tuller found it possible to vary both the magnitudes and ratio of ionic and electronic conductivities over wide limits in the pyrochlore solid solutions $Gd_2(Zr_yTi_{1-y})_2O_7$ through systematic changes in y (16). For large values of y , σ_i increases by orders of magnitude relative to the titanate end member due to increased structural disorder while σ_e decreases sharply due to increases in reduction enthalpy and narrowing of the Ti 3d band. Similar effects can be achieved by doping titanate-rich pyrochlores on the A site or B site (17).

In a previous study we reported on the ionic conducting properties of single-phase fluorite and pyrochlore compositions in the ternary system $ZrO_2-Gd_2O_3-TiO_2$ (18). In this study we report the extent of nonstoichiometry in the fluorite and pyrochlore regions in the system $ZrO_2-Gd_2O_3-TiO_2$. We also report on the phase relations in the three binary systems, $ZrO_2-Gd_2O_3$ (ZG), ZrO_2-TiO_2 (ZT), and $Gd_2O_3-TiO_2$ (GT).

EXPERIMENTAL

High-purity zirconia, gadolinia, and titania (Aldrich) were used as the starting materials. These powders were

dried at 700°C for 15 h and then intimately mixed in the appropriate ratios under acetone, using an agate mortar and pestle. The powders were pressed into pellets (13 mm diameter \times 3 mm) at a pressure of 2000 kg cm⁻². The pellets were calcined at 1000°C for 1 h, heated at 10°C/min to 1500°C, reacted at 1500°C for 32–48 h in air, with intermediate regrinding, and then removed from the furnace and allowed to rapidly cool to room temperature in air. The cooling rate was approximately 250°C/min in the range 1500–1000°C. It is thus unlikely that any changes in phase equilibria will occur on cooling in such a refractory system as this. Phase purity and unit cell parameters were determined by X-ray diffraction (reflection mode, CuK α radiation) using a Philips PW 1830 X-ray diffractometer.

RESULTS

In the ZrO₂–Gd₂O₃ (ZG) binary system, the phase limits are in reasonable accord with the published phase diagram of Rouanet and Foex (8). A small tetragonal ZrO₂ solid solution formed with only a few atom% Gd³⁺. Increasing the Gd₂O₃ content results in a two-phase mixture of tetragonal ZrO₂ solid solution and a defect cubic fluorite phase. On cooling these samples to room temperature and grinding for X-ray investigation, 100% conversion from tetragonal to monoclinic ZrO₂ occurred. A defect fluorite solid solution exists between 20 and 40 at.% Gd³⁺. This structure gradually orders, forming the pyrochlore solid solution, which can be viewed as an ordered superstructure of the fluorite structure and thus has a cubic unit cell parameter double that of the equivalent fluorite composition. This ordered superstructure exists between 40 and 60 at.% Gd³⁺; i.e., it exists around the stoichiometric compound Gd₂Zr₂O₇, which has been reported to disorder to the fluorite structure above \sim 1550°C (19). Increasing the Gd³⁺ content introduces more vacancies into the superstructure lattice, resulting in increasing disorder and a decrease in the intensity of the superstructure reflections until only the peaks characteristic of the defect fluorite structure are visible. The fluorite phase exists between 60 at.% and 65 at.% Gd³⁺. Between 65 and 88 at.% Gd³⁺, there is a two-phase mixture composed of the high-temperature, face-centered cubic form of Gd₂O₃ (C-type) and the fluorite phase. Increasing the amount of Gd₂O₃ creates a single-phase region of the high-temperature cubic Gd₂O₃ in the region 88–95 at.% Gd³⁺. Above 95 at.% Gd³⁺ a two-phase region composed of the C-type Gd₂O₃ and the low-temperature monoclinic form of Gd₂O₃ occurs. The monoclinic form of Gd₂O₃ was observed for 100 at.% Gd³⁺. The unit cell parameters of the monoclinic Gd₂O₃ at 20°C were $a = 14.061$ Å, $b = 3.566$ Å, $c = 8.76$ Å, and $B = 100.1^\circ$. The unit cell parameter, a , of the cubic phases in the ZG system are plotted against at.% Gd³⁺ in Fig. 1. The lattice parameters are not a linear function of Gd₂O₃ especially in the

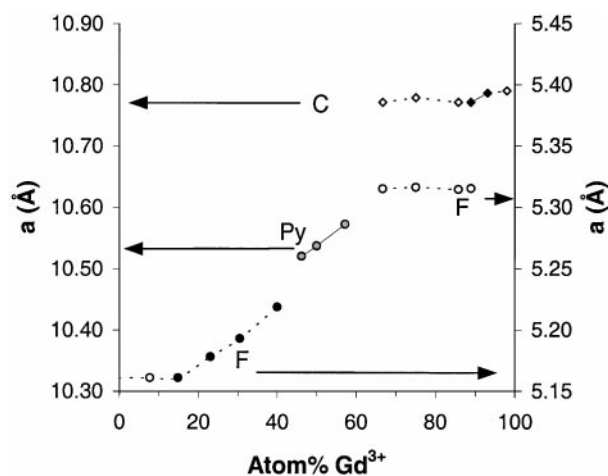


FIG. 1. The unit cell parameter of the cubic phases in the binary ZrO₂–Gd₂O₃ system. All data were obtained at 20°C. Single-phase samples have solid symbols and two-phase samples open symbols. The letters C, R, and F indicate where unit cell parameters correspond to C-type, pyrochlore, and fluorite lattices, respectively.

region of 30–50 at.% Gd³⁺. The curvature has previously been reported in a careful study of the fluorite/pyrochlore region of the ZrO₂–Gd₂O₃ system (19). It is likely that the bend occurs due to the changes in the degree of oxygen vacancy ordering.

For the system Gd₂O₃–TiO₂ (GT) two distinct regions of phase formation were detected as with the Y₂O₃–TiO₂ system (20). The Gd₂TiO₅ line phase is formed at 50 at.% Ti⁴⁺, and a small solid solution region with the Gd₂Ti₂O₇ pyrochlore structure exists between 50 and 53 at.% Ti⁴⁺, in agreement with the phase diagram by Waring and Schneider (14). The Gd₂TiO₅ phase has unit cell parameters $a = 10.4788$ Å, $b = 11.328$ Å, and $c = 3.7547$ Å. The pyrochlore material, Gd₂Ti₂O₇, at 50 at.% Gd³⁺ has a cubic unit cell parameter $a = 10.1860$ Å. No other regions of solid solubility were detected between Gd₂O₃ and TiO₂. Phase relations determined for the ZT system in this study are also in accord with previous literature and are reported elsewhere in the study of phase relations in the system ZrO₂–Y₂O₃–TiO₂ (20).

The ternary phase diagram is shown in Fig. 2. The single-phase, two-phase, and three-phase regions are indicated. No new phases are observed in the ternary system, and apart from the defect fluorite system and the pyrochlore system, none of the binary systems extend significantly into the ternary system.

We have determined that a large nonstoichiometric cubic solid solution exists around the stoichiometric solid solution system Gd₂Zr₂O₇–Gd₂Ti₂O₇ that was reported by Moon and Tuller (15), Fig. 2. The defect cubic fluorite region at the low Gd³⁺ end of the phase diagram extends to 10 at.% Ti⁴⁺ in the ternary system containing 30 at.% Gd³⁺. The pyrochlore structure forms a complete solid

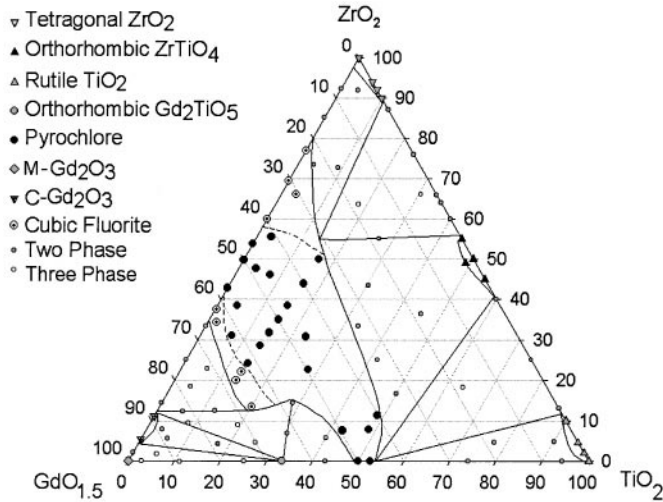


FIG. 2. The experimentally determined ternary phase diagram for the ternary system ZrO_2 - Gd_2O_3 - TiO_2 at 1500°C. The dashed line indicates the approximate position of the gradual transition from pyrochlore to fluorite structure within the cubic pyrochlore/fluorite phase field.

solution between the ZG system and the GT system, around the stoichiometric compositions containing 50 at.% Gd^{3+} . The maximum extent of the deviation from ideal M_4O_7 stoichiometry in the ternary system is attained for compositions containing around 15 at.% Ti^{4+} , between the limits of 33 and 63 at.% Gd^{3+} .

Increasing the nonstoichiometry further in the ternary system causes sufficient disordering of the cation and anion sublattices of the pyrochlore structure to result in the disappearance of the superstructure reflections and resulting in the fluorite average structure occurring. As with the binary ZG system, no evidence of a two-phase region between the pyrochlore and fluorite regions was found. The transition

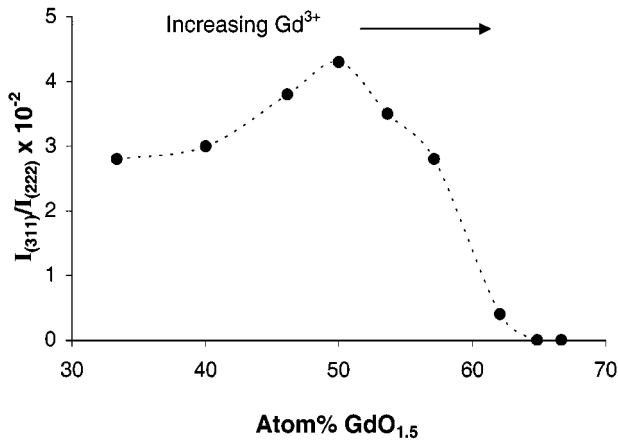


FIG. 3. Ratio of the (311) peak intensity to the (222) peak intensity at 20°C as a function of Gd^{3+} content for pyrochlore and fluorite compositions containing 20 mol% TiO_2 .

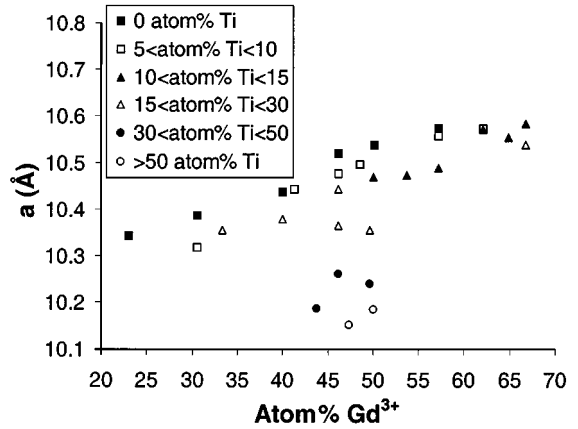


FIG. 4. The general trend in the unit cell parameter of single-phase compositions in the system ZrO_2 - Gd_2O_3 - TiO_2 versus at.% Gd^{3+} . The unit cell parameters of the fluorite compositions have been plotted as $2a$ so that they may be compared to the larger cells of the pyrochlore compositions.

from the pyrochlore structure to the fluorite structure is thus a continuous order-disorder transition. Figure 3 shows the ratio of the superstructure (311) reflection intensity to the fluorite-related (222) reflection intensity for pyrochlore compositions containing 20 mol% TiO_2 . This line joins the compositions $8 GdO_{1.5}:1 TiO_2$ to $8ZrO_2:2TiO_2$, although in the region of interest the at.% Ti is $15(\pm 2)\%$. This intensity ratio can be seen to increase from the limit of single-phase pyrochlore formation (33 at.% Gd^{3+}) up to the stoichiometric composition containing 50 at.% Gd^{3+} . The ratio of the intensities then decreases rapidly as the amount of disorder caused by the increase in aliovalent Gd^{3+} increases. When the (311) reflection is not visible the average structure is now fluorite rather than pyrochlore and the ratio of the intensities is zero.

The limiting composition for the defect cubic fluorite structure with increasing $GdO_{1.5}$ and thus increasing deviation in stoichiometry from M_4O_7 is the composition $Zr_{0.13}Gd_{0.67}Ti_{0.20}O_{1.67}$. This is similar to the extent of the single phase, defect fluorite structure in the ZrO_2 - Y_2O_3 - TiO_2 system, for which the composition $Zr_{0.21}Y_{0.62}Ti_{0.17}O_{1.69}$ was prepared (20). Cell parameters for some of the stoichiometric and nonstoichiometric pyrochlore and fluorite samples of the ternary system are reported elsewhere (18); however, the unit cell parameters for all of the single-phase compositions prepared are shown plotted against at.% Gd^{3+} in Fig. 4 and against atom% Ti^{4+} in Fig. 5. Figure 4 shows that the unit cell parameter increases with increasing Gd^{3+} content and that increasing the Ti^{4+} content lowers the unit cell size. Figure 5 shows the same trends in the unit cell parameter as Figure 4; i.e., the unit cell size increases with Gd^{3+} content and decreases with increasing Ti^{4+} content. The unit cell parameters for the end members $Gd_2Zr_2O_7$ and $Gd_2Ti_2O_7$ are 10.52 and

