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Effect of $\text{Pr}^{3+}/\text{Pr}^{4+}$ ratio on the oxygen ion transport and thermomechanical properties of the pyrochlore and fluorite phases in the $\text{ZrO}_2\text{--Pr}_2\text{O}_3$ system

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ABSTRACT

This paper examines the effect of the $\text{Pr}^{3+}/\text{Pr}^{4+}$ ratio on the mechanism of ionic and electronic transport in the $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ ($x = 0.15$), $\text{Pr}_2\text{Zr}_2\text{O}_7$, and $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 0.1$) pyrochlore phases and Pr_3ZrO_x with the fluorite structure and on the behavior of their thermal expansion coefficient (TEC). The solid solutions were prepared through coprecipitation followed by firing of the green compacts in air at a high temperature of 1550 °C for 4 h. The $\text{Pr}^{3+}/\text{Pr}^{4+}$ ratio was shown to decrease in going from the $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ ($x = 0.15$), $\text{Pr}_2\text{Zr}_2\text{O}_7$, and $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 0.1$) pyrochlores to the Pr_3ZrO_x fluorite, leading to changes in the conductivity type from mixed (ionic–electronic) to electronic and in the color of the materials from beige to black and to an anomalous deviation of the TEC from linearity in fluorite Pr_3ZrO_x , i.e. at the highest Pr^{4+} content. According to impedance spectroscopy results, $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ with $x = 0.15$ has purely oxide-ion conductivity (3×10^{-3} S/cm at 1000 °C) in a wide range of oxygen partial pressures: from 10^{-10} to 10^2 Pa. With increasing Pr content, p-type electronic conductivity becomes significant, reaching a maximum in fluorite Pr_3ZrO_x : ~ 0.5 S/cm at 1000 °C. According to XPS data, all pyrochlore samples $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ ($x = 0.15$), $\text{Pr}_2\text{Zr}_2\text{O}_7$ and $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 0.1$) contain only Pr^{3+} at room temperature, whereas Pr_3ZrO_x contains both Pr^{3+} and Pr^{4+} . The considerable deviation of the TEC of Pr_3ZrO_x from linearity above 500 °C is due to partial reduction of Pr^{4+} . The reduction process $\text{Pr}^{4+} + e^- \rightarrow \text{Pr}^{3+}$ followed by oxygen release in the range 500–1100 °C has been identified in Pr_3ZrO_x by thermal analysis and mass spectrometry in a He atmosphere.

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Introduction

Many undoped and acceptor-doped $\text{Ln}_2\text{M}_2\text{O}_7$ ($\text{Ln} = \text{La}–\text{Lu}$; $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$) pyrochlores are widely known oxygen vacancy conductors. Oxygen vacancy generation in these materials has been extensively discussed in the literature [1–10]. Their main potential application is solid electrolytes for SOFCs because they are close in oxide ion conductivity to the conventional ZrO_2 -based solid electrolytes doped with 10–15 mol % Y_2O_3 or Sc_2O_3 [11]. Among the pyrochlore zirconates, the $\text{Ln}_2\text{Zr}_2\text{O}_7$ ($\text{Ln} = \text{Ce}, \text{Pr}$) zirconates, containing 3+/4+ variable-valence cations (Ce and Pr) are the least studied. The main reason for this is that during synthesis in air the Ln^{3+} in the $\text{Ln}_2\text{Zr}_2\text{O}_7$ ($\text{Ln} = \text{Ce}, \text{Pr}$) pyrochlores as a rule partially oxidizes to Ln^{4+} [12–15], which leads to coexistence of the Ln^{3+} and Ln^{4+} in the A site of $\text{Ln}_2\text{Zr}_2\text{O}_7$ pyrochlores:



This process limits the use of these pyrochlores as solid electrolytes, but they can be studied as MIECs for SOFC electrodes.

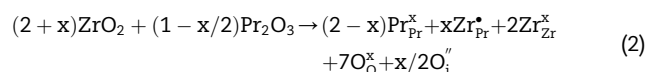
The Pr and Tb cations are the most stable in the pyrochlore structure among the known 3+/4+ variable-valence rare-earth cations [16]. In particular, $\text{Tb}_2\text{Ti}_2\text{O}_7$ and $\text{Tb}_2\text{Hf}_2\text{O}_7$ can be synthesized readily in air and the only compound in the $\text{Tb}_2\text{O}_3–\text{ZrO}_2$ system is fluorite $\text{Tb}_2\text{Zr}_2\text{O}_7$ ($\text{TbZrO}_{4-\delta}$) [17,18]. $\text{Pr}_2\text{Zr}_2\text{O}_7$ can be prepared rather easily both by solid-state reaction and using solution techniques followed by high-temperature firing in air [15,19,20]. Undoped $\text{Ce}_2\text{Zr}_2\text{O}_7$ can only be synthesized under reducing conditions, and subsequent exposure of this material to air leads to the oxidation of Ce^{3+} to Ce^{4+} [13,14]. Thus, because of the low potential of $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$ oxidation (1.44–1.7 V), $\text{Ce}_2\text{Zr}_2\text{O}_7$ cannot be used as a SOFC material.

It should be emphasized that ionic and electronic transport processes in the $\text{Pr}_2\text{O}_3–\text{ZrO}_2$ system have been the subject of a limited number of reports [15,19–22]. In connection with this, studies of $\text{Pr}_x\text{Ce}_{1-x}\text{O}_{2-\delta}$ ($x = 0, 0.01, 0.1, 0.2$) as potential SOFC cathodes [23–25] are of interest, where the oxide ion conductivity was measured as a function of oxygen partial pressure, the thermomechanical behavior of the materials was investigated, and anomalous thermal expansion was found at temperatures $T > 500–600$ °C in air, which was tentatively attributed to the reduction of Pr^{4+} to Pr^{3+} at these temperatures. This was accompanied by a considerable rise in electronic conductivity at elevated temperatures.

Because of this, we investigated not only the conductivity (as a function of oxygen partial pressure) but also the thermomechanical properties of pyrochlore-like $\text{Pr}_2\text{O}_3–\text{ZrO}_2$ solid solutions in the rather narrow (~6 mol %) isomorphous miscibility range of $\text{Pr}_{2\pm x}\text{Zr}_{2\pm x}\text{O}_{7\pm\delta}$ and those of a Pr-rich fluorite solid solution.

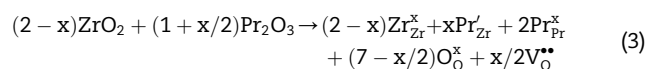
The following compositions were studied:

pyrochlore $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ ($x = 0.15$), containing excess Zr^{4+} on the Pr^{3+} site, as a potential interstitial conductor, in which the formation of oxygen interstitials can be represented (in Kröger–Vink notation) by Eq. 2



the pyrochlore compound $\text{Pr}_2\text{Zr}_2\text{O}_7$;

pyrochlore $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 0.1$), containing excess Pr^{3+} on the Zr^{4+} site, as a potential oxygen vacancy conductor, in which oxygen vacancy formation can be described by Eq. 3



and a $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 1$) Pr-rich fluorite solid solution.

Experimental

Using coprecipitation followed by heat treatment at 1550 °C for 4 h, we prepared pyrochlore- and fluorite-like PrZrO solid solutions containing 30, 33.3, 35.5, and 60 mol % Pr_2O_3 [20], which corresponds to the following compositions: $(\text{Pr}_{2-x}\text{Zr}_x)\text{Zr}_2\text{O}_{7+x/2}$ ($x = 0.15$), $\text{Pr}_2\text{Zr}_2\text{O}_7$, $\text{Pr}_2(\text{Zr}_{2-x}\text{Pr}_x)\text{O}_{7-x/2}$ ($x = 0.1, 1$).

The starting chemicals used were PrCl_3 and $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ powders, which were dissolved in distilled water. Solution concentrations were determined gravimetrically. The concentrations of the chloride solutions were 0.09 M (Pr) and 1.085 M (Zr). All the PrZrO solid solutions were synthesized through reverse precipitation (pH 11.6–11.2), by adding titrated praseodymium chloride and zirconium chloride solutions to aqueous ammonia. After the formation of light green gel-like precipitates, they were aged at room temperature for 4 h. Next, the mother liquor was decanted and the rest was centrifuged. The precipitate was washed with warm water five times to remove Cl^- ions and then dried in air for 66 h at 75 °C, which allowed it to remain light green in color, typical of trivalent Pr. The development of a brown color during drying indicates the formation of Pr^{4+} centers.

The hydroxide precursors thus prepared were pressed at 259 (first composition) or 216 MPa (last three compositions) into pellets, which were then fired at 1550 °C for 4 h.

The density of the resultant samples was determined by measuring their mass and dimensions and ranged from 85 to 90% of their X-ray density [20]. All of the synthesized solid solutions were characterized by X-ray diffraction (XRD) on a DRON-3M (filtered CuK_α radiation, step scan mode with a step of 0.05°, angular range $2\theta = 10–100^\circ$, Rietveld refinement).

The oxidation state of the praseodymium in the solid solutions was determined by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis Ultra DLD spectrometer using a monochromatic Al $\text{K}\alpha$ X-ray source (1486.6 eV, 150 W). High-resolution spectra were acquired at 40 eV pass energy. The analysis area was about 300×700 μm . The binding energy scale of the spectrometer was preliminary calibrated using the following lines of standards (cleaned by ion sputtering): Au $4f_{5/2}$ at 83.96 eV, Cu $2p_{3/2}$ at 932.62 eV, and Ag $3d_{5/2}$ at 368.21 eV. A Kratos charge neutralizer system was used. As the binding-energy-scale reference, we used the C 1s level (284.6 eV) arising from the carbon adsorbed on the sample surface.

Thermal analysis was carried out using a Netzsch STA 449C system in combination with an AEOLOS-32 mass

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