Viewpoint Paper

# Unraveling the defect chemistry and proton uptake of yttrium-doped barium zirconate

Yoshihiro Yamazaki, Chih-Kai Yang and Sossina M. Haile*

*Materials Science, California Institute of Technology, 1200 E. California Blvd., Pasadena, CA 91125, USA*

**Abstract**—A review of the experimental literature documenting water uptake in yttrium-doped barium zirconate in combination with new results obtained here show that much of the observed scatter can be explained in terms of barium deficiency, which furthermore induces a lowering in cell volume. In addition, through a comparison of weight changes under regular and heavy water vapor pressure, strong evidence is found for bulk oxidation of the oxide by water simultaneous with hydration.
© 2011 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

## 1. Introduction

Amongst proton-conducting oxides, yttrium-doped barium zirconate (BYZ) has emerged as a highly attractive material because of the combination of high conductivity and excellent chemical stability it affords [1–3]. The cubic nature of this perovskite additionally suggests a simplicity that is appealing both scientifically and technologically. Furthermore, although the refractory characteristics introduce processing challenges, viable approaches have recently been developed for achieving high-density and large-grained materials at accessible sintering temperatures [4,5]. Such processing not only reduces fabrication costs but, by decreasing the number density of high-resistance grain boundaries, also increases the overall material conductivity. Despite this progress, there remains considerable scatter in the reported properties of yttrium-doped barium zirconate as related to its bulk defect chemistry and hydration characteristics, factors that must be fully characterized if one is to realize electrochemical devices such as fuel cells, electrolyzers and hydrogen separation membranes based on this material. The present contribution aims to assess the source of these discrepancies. From a review of the literature and new data presented here, we conclude that substantial variations in material stoichiometry can account for some of the scatter. Simultaneously, the methods of evaluating water uptake and extracting thermodynamic data must be carefully addressed for ensuring reliable and meaningful results.

## 2. Defect chemistry and phase behavior

Proton incorporation into perovskites relies on first doping the material so as create oxygen vacancies. In the specific case of yttrium-doped barium zirconate, one aims to replace a portion of the $Zr^{4+}$ ions with $Y^{3+}$ ions, which, for charge balance reasons, implies the generation of the desired oxygen vacancies. The dopant incorporation reaction is formally written, in Kroger–Vink notation, as:

$$2Zr_{Zr}^{\times} + O_O^{\times} + Y_2O_3 \leftrightarrow 2Y_{Zr}' + V_O^{\cdot\cdot} + 2ZrO_2 \tag{1}$$
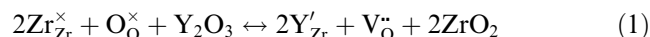
In the ideally doped material, all of the barium (or A) sites remain fully occupied by $Ba^{2+}$ ions and all of the zirconium (or B) sites are fully occupied by a combination of $Zr^{4+}$ and $Y^{3+}$ ions, and the molar ratio $[Ba]/([Zr] + [Y])$ is 1. It has become increasingly recognized that this ideal scenario is relatively easily violated under processing conditions (extreme temperatures and prolonged times) that result in barium evaporation. In such a case, by definition, the molar ratio $[Ba]/([Zr] + [Y])$ falls in a global sense below 1. Several defect chemical scenarios by which the material may accommodate this modification to the overall stoichiometry can be envisioned. A step back from the local defect chemistry to the global phase behavior provides some indication as to which scenario predominates.
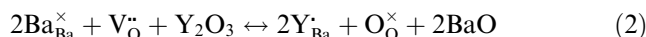
Figure 1 shows the phase behavior in the $BaO–ZrO_2–YO_{1.5}$ system. Pseudo–ternary diagrams for 1600 °C as reported by Imashuku *et al.* [6] and by Yamazaki *et al.* [7] are presented, along with the pseudo–binary diagram in the $BaO–ZrO_2$ system as reported by Paschoal *et al.* [8].

* Corresponding author. E-mail: smhaile@caltech.edu

A horizontal line from $0.5BaO \cdot 0.5ZrO_2$ to $0.5BaO \cdot 0.5YO_{1.5}$ in the pseudo–ternary diagrams corresponds to the set of compositions of the ideally doped material, whereas the region just below this line corresponds to the barium-deficient compositions. The global phase behavior indicates that the yttrium solubility in the ideal case is ∼30 at.%, whereas in the barium-deficient case it reaches ∼50 at.%. The phase behavior further indicates that no barium excess is tolerated in the perovskite structure, irrespective of the [Zr]/[Y] molar ratio. The implication is that any hypothetical set of defects that could accommodate barium excess (e.g. Zr and O vacancy pairs or Ba and O interstitial pairs) are thermodynamically unfavorable. While not directly relevant to the hydration characteristics of the perovskite phase, it is noteworthy that such compositions yield secondary phases such as BaO and $Ba_2ZrO_4$ [8] that can assist in sintering, but readily form hydroxides [9,10] and carbonates [7,11] upon reaction with atmospheric water and carbon dioxide, inducing mechanical disintegration of sintered compacts. It is also of some significance that at very high



**Figure 1.** Phase behavior in the $BaO–ZrO_2–YO_{1.5}$ pseudo–ternary system: pseudo–ternary phase diagrams at 1600 °C after (a) Imashuku et al. [6] and (b) Yamazaki et al. [7]; and (c) pseudo–binary phase diagram in the $BaO–ZrO_2$ system after Paschoal et al. [8]. Reproduced with permission from Refs. [6], [7] and [8], respectively. In (a) "BZY424" is a yttrium-rich perovskite-like phase. In (b) inset shows expansion of circled region.
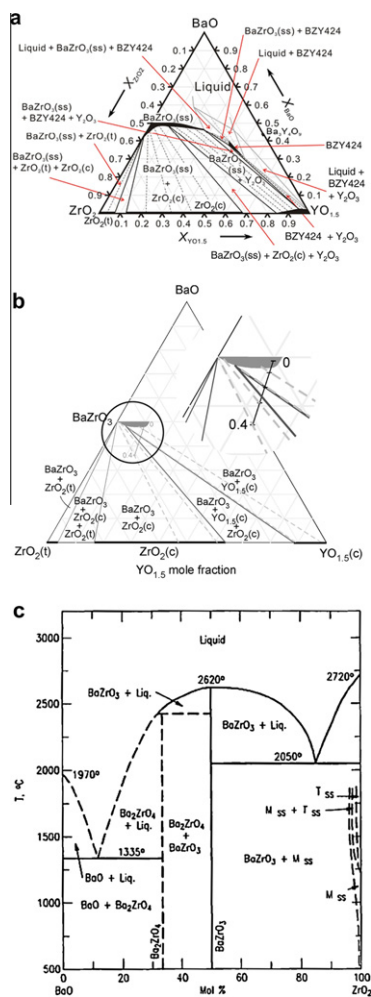
yttrium concentrations, perovskite phase separation between yttrium-rich and yttrium-poor compositions occurs, as has been reported also for lower temperature studies [6,12–14].

Returning to the characteristics of the primary perovskite phase, the observation that compositions with $[Ba]/([Zr] + [Y]) < 1$ form single-phase perovskites does not immediately reveal the local defect chemistry. In an earlier work by the present authors [7], it was observed that undoped barium zirconate does not tolerate detectable levels of barium deficiencies, similar to the behavior of barium cerate [11]. This feature of the $BaO–ZrO_2$ psuedo–binary system was indeed reported much earlier by Paschoal et al. [8]. Accepting that undoped barium zirconate does not tolerate barium deficiencies, the single-phase behavior of the doped systems can be directly linked to the presence of the dopant. The more comprehensive phase diagram study of Imashuku et al. [6], however, is in disagreement with the observations in Refs. [7,8], and these authors find that even $0.9BaO \cdot 1.0ZrO_2$ yields single-phase perovskite, suggesting that the dopant is not essential to the stabilization of the perovskite phase. Given these discrepancies, we turn to the crystallographic behavior of yttrium-doped barium zirconate to give insight into the local defect chemistry in barium-deficient compositions.

For an ideal composition with dopant incorporation according to reaction (1), one expects the cell constant of the cubic perovskite phase to expand monotically as the $Zr^{4+}$ cation is replaced with the larger $Y^{3+}$ cation ($R^{VI}_{Zr^{4+}} = 0.72$ Å; $R^{VI}_{Y^{3+}} = 0.90$ Å [15]). Now consider the impact of barium deficiency. For the undoped material, the single-phase perovskite, should it form, would either incorporate Zr and O interstitials, an unlikely scenario given the high charge associated with an interstitial Zr ion, or Ba and O vacancies, a much more plausible situation. For the more important case of the doped system, the preponderance of the literature indicates that, when $[Ba]/([Zr] + [Y]) < 1$, rather than generate Ba and O vacancy pairs, the perovskite adopts a structure in which yttrium is partitioned over both the A and B cation sites [7,14]. Specifically, in addition to reaction (1), dopant incorporation occurs via the following reaction:

$$2Ba^{\times}_{Ba} + V^{\cdot\cdot}_O + Y_2O_3 \leftrightarrow 2Y'_{Ba} + O^{\times}_O + 2BaO \qquad (2)$$

Because yttrium is smaller than barium ($R^{IX}_{Y^{3+}} = 1.08$ Å; $R^{XII}_{Ba^{2+}} = 1.62$ Å [15]), partitioning of the dopant over the two sites can be expected to decrease the cell volume relative to a composition in which $[Ba]/([Zr] + [Y]) = 1$. Such behavior is indeed observed in the case of $Ba_{1-x}Zr_{0.8}Y_{0.2}O_{3-\delta}$ (Fig. 2a) [7]. The single-phase perovskite is maintained to a barium deficiency of $x = 0.082$, where this is the post-synthesis, measured value as opposed to the nominal value. Across the single-phase region, the cell constant decreases monotonically with increasing $x$, with greatest sensitivity at small values of $x$. Such a reduction in cell constant supports the proposition of dopant partitioning in barium-deficient stoichiometries. It does not, however, rule out the possibility of some accommodation of barium deficiency via the formation of barium and oxygen vacancies pairs. A change in the defect chemistry in this manner could also induce a reduction in cell volume, but presumably to a much lesser