Defect Chemistry of Yttrium-Doped Barium Zirconate: A Thermodynamic Analysis of Water Uptake

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Thermogravimetry has been used to evaluate the equilibrium constants of the water incorporation reaction in yttrium-doped $BaZrO_3$ with 20−40% yttrium in the temperature range 50−1000 °C under a water partial pressure of 0.023 atm. The constants, calculated under the assumption of a negligible hole concentration, were found to be linear in the Arrhenius representation only at low temperatures ($\leq$500 °C). Nonlinearity at high temperatures is attributed to the occurrence of electronic defects. The hydration enthalpies determined here range from −22 to −26 kJ mol^{-1} and are substantially smaller in magnitude than those reported previously. The difference is a direct result of the different temperature ranges employed, where previous studies have utilized higher temperature thermogravimetric measurements, despite the inapplicability of the assumption of a negligible hole concentration. The hydration entropies measured in this work, around −40 J K^{-1} mol^{-1}, are similarly smaller in magnitude than those previously reported and are considerably smaller than what would be expected from the complete loss of entropy of vapor-phase H_2O upon dissolution. This result suggests that substantial entropy is introduced into the oxide as a consequence of the hydration. The hydration reaction constants are largely independent of yttrium concentration, in agreement with earlier reports.

1. Introduction

Acceptor-doped perovskites have received considerable attention as solid-state proton conductors for a range of electrochemical applications, including fuel cells, gas sensors, and hydrogen pumps.[1,2] Such materials are particularly promising as electrolytes for intermediate temperature (400−700 °C) solid oxide fuel cells (SOFCs), which alleviate many of the material lifetime and cyclability challenges arising from the very high temperature operation, 800−1000 °C, of conventional zirconia-based SOFCs.[3] Of known proton conducting oxides, yttrium-doped barium zirconate (BYZ) is particularly attractive because it combines high proton conductivity with excellent mechanical strength and chemical stability under CO_2-containing atmospheres.[4,5] Indeed, the bulk (or grain interior) conductivity of BYZ is, at temperatures of about 600 °C, comparable to that of gadolinium-doped ceria, one of the highest conductivity oxide ion conductors, and exceeds it below 500 °C.[5]

In the present work, we turn our attention not directly to the transport properties of BYZ, but rather, to its defect chemistry and the thermodynamics thereof. In contrast to oxygen ion conductors, which typically have a constant carrier (oxygen vacancy) concentration under the conditions of interest, BYZ displays complex defect thermodynamics involving multiple mobile species. Doping with trivalent yttrium onto the tetravalent zirconium in barium zirconate generates oxygen vacancies as charge compensating defects. By means of treatment in water vapor, these vacancies may be replaced by protons which occur in the form of hydroxyl groups residing on oxygen sites (the water incorporation reaction[6]). At high temperatures, water is expelled from the structure,[7] and at even higher temperatures, under oxidizing atmospheres, oxygen vacancies are consumed and electronic holes are generated (the oxidation reaction[8]). Thus, protons, oxygen vacancies, and electronic holes can all coexist, with their concentrations dependent on dopant concentration, temperature, oxygen partial pressure, and water partial pressure.

The fundamental parameters describing the defect chemistry of any material are captured in the equilibrium constants associated with the relevant defect creation reactions. Thus, knowledge of these constants permits one to fully describe the defect concentrations in a given material at any given set of experimental conditions.[9,10] Although such parameters are therefore highly desirable, experimental determination of the equilibrium constants for defect creation in proton-conducting perovskites, and BYZ in particular, has not been systematically pursued. There are no reports of the oxidation reaction constant for BYZ at any dopant concentration, and only two measurements of the hydration reaction constants

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appear in the literature.[11,12] The scarcity of such data may reflect the significant processing challenges associated with the preparation of BYZ, resulting from its highly refractory nature.[13] As discussed in greater detail below, although the existing measurements of the hydration reaction constants, carried out first by Kreuer[4,12] and subsequently by Schober and Bohn,[11] provide a useful starting point for evaluating the defect chemistry of BYZ, the analyses were carried out neglecting the potential impact of the oxidation reaction, which cannot be readily justified for the high temperatures at which the experimental (thermogravimetric) data were acquired. Indeed, in the specific case of $BaZr_{0.8}Y_{0.2}O_{3-\delta}$, even under a high water partial pressure of 0.042 atm (and ambient oxygen partial pressure), measurable hole conductivity has been reported by Nomura and Kageyama at 600 °C,[19] with the ionic transference number falling to below 0.5 at these conditions.

In the present work, the influence of the temperature range of data analysis on the apparent equilibrium reaction constant for hydration is examined using thermogravimetric data collected under controlled water partial pressures. It is concluded that extraction of the thermodynamic parameters is justified only using the low temperature data, at which the assumption of negligible electronic defect concentration is valid. The significance of the extracted parameters as well as their dependence on dopant concentration is discussed.

2. Experimental Section

Undoped and yttrium-doped barium zirconates, $Ba(Zr_{1-x}Y_x)O_{3-\delta}$ (x = 0, 0.2, 0.3, and 0.4), were prepared using glycine nitrate combustion synthesis[14] by a procedure optimized for reproducibly obtaining high-conductivity compacts.[13] Hereafter, the samples with x = 0.2, 0.3, and 0.4 are termed BYZ20, BYZ30 and BYZ40, respectively. Starting materials were high-purity $Ba(NO_3)_2$ (Alfa Aesar 99.9% purity), $Y(NO_3)_3 \cdot 6H_2O$ (Alfa Aesar, 99.9% purity), and $ZrO(NO_3)_2 \cdot yH_2O$ (Alfa Aesar 99.9% purity, where y = 2.3). Powders obtained from the synthesis were calcined at 1200 °C for 5 h under air and subsequently attritor-milled at 500 rpm for 5 h.

The structure of the barium zirconate powders was confirmed to be single-phase perovskite by X-ray powder diffraction (Phillips X'Pert Pro). X-ray patterns were also utilized to determine lattice parameters by Rietveld refinement as implemented in the X'Pert Plus software. The specific surface area of the samples, which can influence water uptake kinetics and potentially even thermodynamics, was determined via a conventional nitrogen absorption technique, the Brunauer−Emmett−Teller method, at liquid nitrogen temperature using a Micromeritics ASAP 2010. Prior to measurement, samples were degassed for 16 h with flowing ultrahigh-purity nitrogen at 80 °C.

Thermogravimetric analysis was performed using a Netzsch STA (simultaneous thermal analyzer) Jupiter 449 C. The as-prepared powders were heated to 1000 °C and held there for 0.5 h under dry nitrogen (99.995% purity) to remove water from the structure and also possible surface carbon dioxide. The sample gas was then
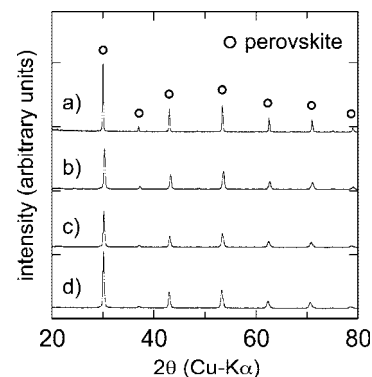
Figure 1. X-ray powder diffraction of (a) undoped $BaZrO_3$, (b) BYZ20, (c) BYZ30, and (d) BYZ40 powders.
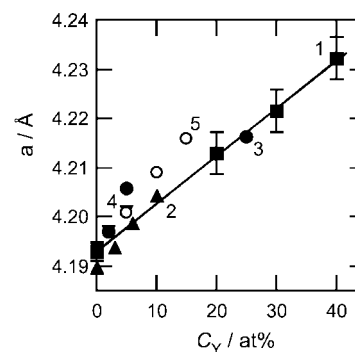
Figure 2. Lattice parameter of cubic yttrium-doped barium zirconate system together with previous works: 1-this work; 2-Schober and Bohn;[11] 3-Kreuer et al.;[12] 4-Omata et al.;[15] and 5-Iguchi et al.[16]

saturated with water (P_{H_2O} = 0.023 atm), and the weight increase was recorded upon cooling. Data were collected every 100 °C from 1000 °C to room temperature, with a 2 h stabilization time at each temperature.

3. Results

The X-ray diffraction patterns of undoped $BaZrO_3$ and BYZ20−40 powders are shown in Figure 1. For each pattern, only the perovskite phase is evident; no precipitates of a second phase are apparent, even at the high dopant concentrations utilized. The lattice constant of barium zirconate as a function of yttrium concentration is presented in Figure 2 and compared to those reported by Schober and Bohn,[11] Kreuer et al.,[12] Omata et al.,[15] and Iguchi et al.[16] The refined lattice constant of undoped barium zirconate is 4.193(1) Å, which compares well with the value (4.1973 Å) reported in the ICSD database, no. 90049. The lattice constant increases linearly with increasing yttrium concentration (as a result of the larger ionic radius of Y^{3+} relative to Zr^{4+}), further suggesting that the solubility limit of yttrium into barium zirconate has not been reached. In contrast to these results, Yamaguchi et al. reported phase separation at intermediate dopant concentrations between 8 and 40% yttrium.[17] A more

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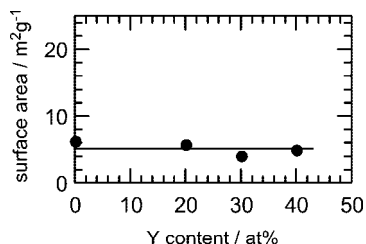
Figure 3. Specific surface area of as-prepared BYZ powders as a function of yttrium content.
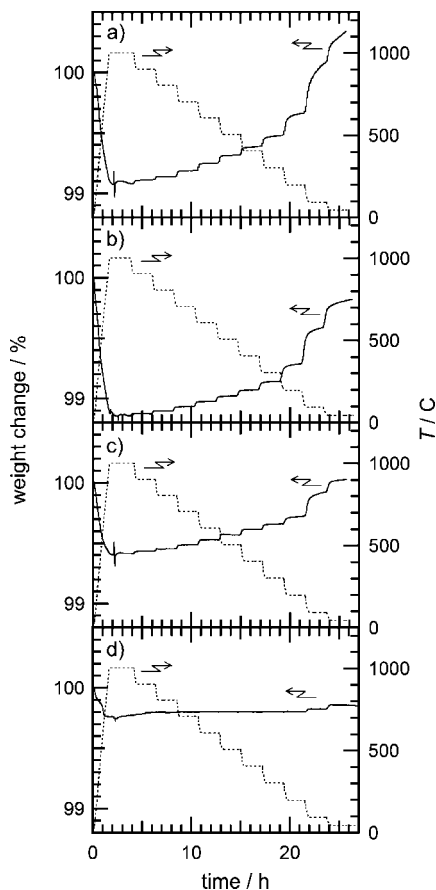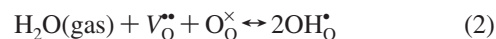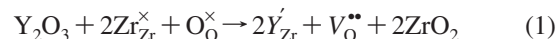

Figure 4. Weight change of (a) BYZ40, (b) BYZ30, (c) BYZ20, and (d) undoped BaZrO$_3$ samples and temperature as a function of time under water partial pressure of 0.023 atm.

detailed evaluation of the diffraction patterns may have also led to such a conclusion, but is beyond the scope of the present work.

The specific surface area values and the weight change results obtained from the thermogravimetric analysis are presented in Figures 3 and 4, respectively, for all four compositions examined (P_{H_2O} = 0.023 atm). It is evident that the synthesis procedure yields materials with comparable specific surface areas for dopant concentrations. The water uptake behavior is also similar for all compositions. In all cases, the sample weight becomes constant within 2 h at all temperatures except 50 and 100 °C, suggesting that at higher temperatures, the bulk proton (and oxygen) concentrations have equilibrated. For the lower temperatures, it is possible to estimate the deviation of each final measurement from the equilibrium value by taking the weight to relax to the

equilibrium value according to $(\bar{w} - w_1)/w_0 = -8\pi^{-2}$ $\exp(-t/\tau)$,[18] as would be expected for a diffusion-limited process, where $\bar{w}$ is the time-averaged weight of the sample, w_0 and w_1 are the weights before and after the equilibration, t is time, and τ is the relaxation period. From this estimate, we conclude that the ultimate weight gain at 100 °C is only 2−7% greater than what is observed in the 2 h equilibration period. This level of error is sufficiently small that extended equilibration periods were deemed unnecessary.

As is now well-established and was briefly introduced above, water uptake in doped barium zirconate under humid atmospheres occurs as a result of the filling of vacancies generated by doping. The relevant reactions are given as

$$Y_2O_3 + 2Zr_{Zr}^{\times} + O_O^{\times} \rightarrow 2Y'_{Zr} + V_O^{\bullet\bullet} + 2ZrO_2 \qquad (1)$$

$$H_2O(gas) + V_O^{\bullet\bullet} + O_O^{\times} \leftrightarrow 2OH_O^{\bullet} \qquad (2)$$

where the first reaction describes vacancy creation; the second, the water uptake reaction; and both expressions are written using Kröger−Vink notation. The second expression provides a means of evaluating the (presumed) proton concentration from the thermal gravimetric data.

As evident from Figure 4d, undoped barium zirconate displays detectable weight gain at low temperatures; specifically, an amount of ∼0.07% at 50 °C. The absence of extrinsic oxygen vacancies and, thus, an obvious bulk water incorporation mechanism for this material as well as the preponderance of this effect at low temperatures suggests that the weight gain is due to surface adsorbed water. Alternatively, the water uptake may reflect the presence of background acceptor impurities. Assuming these effects are independent of yttrium concentration, an assumption justified by the composition independent specific surface area (Figure 3) and the comparable processing methodologies, the weight change observed for undoped barium zirconate is subtracted from that measured for the doped compositions to give what is presumed to be the actual proton content due to yttrium doping for further analysis.

Analysis of the raw data in Figure 4 (corrected for the presumed surface adsorbed water) according to the reaction of eq 2 yields the proton concentrations summarized in Figure 5 as a function of temperature for both the doped and undoped samples. Literature results for BYZ10 and BYZ20 are also presented for comparison.[11,12] At 50 °C, the proton concentrations in BYZ20, 30, and 40 are 0.178, 0.278, and 0.372 [OH]/[Ba], respectively. These values are close to those for full saturation of protons into the structure, 0.2, 0.3, and 0.4, respectively, and corresponding to one proton per yttrium dopant ion. The high extent of proton uptake is a strong indicator that the yttrium dopant is largely incorporated onto the Zr rather than Ba site and further suggests that deviations from equilibrium for the lower temperature measurements (due to slow kinetics) are minimal. Overall, the proton concentration gradually decreases with increasing tempera-

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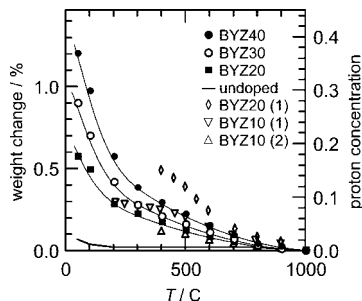
Figure 5. Weight change and proton concentration in BYZ samples as functions of temperature and dopant concentration in comparison with previous works: (1) Kreuer et al.;[12] (2) Schober and Bohn.[11]

ture, whereas it increases with increasing yttrium content, in agreement with the general expectations of the defect chemistry (eqs 1, 2).

Turning to the previously published literature data, Schober and Bohn[11] report proton concentrations in BYZ10 at similar water partial pressures, $P_{H_2O} \approx 0.02$ atm, that are slightly smaller than that observed here in BYZ20 and are thus entirely consistent with the trend toward lower water uptake with lower dopant concentrations. On the other hand, the proton concentration in BYZ10 and BYZ20 determined by Kreuer et al.,[12] also at a comparable water partial pressure, P_{H_2O} (= 0.023 atm), is much larger than that reported by Schober and Bohn[11] in BYZ10 and also that in BYZ20 determined in this study. In light of these experimental discrepancies, it is of some value to discuss differences in experimental methods. In the case of Schober and Bohn,[11] thermogravimetric analysis of BYZ10 was carried out isothermally in a manner similar to that described here, although the equilibration time at each temperature was not specified; neither is it clear whether the data were collected on heating or cooling. Nevertheless, the isothermal nature of the studies suggests that equilibration was achieved. In the study by Kreuer et al.,[12] the data were collected under constant cooling (at an unspecified rate), and the raw data reveal significant hysteresis between weight values recorded on cooling and those recorded on heating. Surprisingly, both sets of data imply high water content, and the smaller weight values (those recorded on cooling) are shown in Figure 5. If the data reported by Kreuer do not represent equilibrium, they would be expected to reflect an underestimation of the proton content, and the discrepancies (i.e., the large values) cannot be easily explained.

4. Discussion

Under the implied assumption that water uptake is the sole cause of weight change, the data presented in Figure 5 can be used to evaluate the thermodynamics of defect creation in doped barium zirconate. In particular, the equilibrium constant, K_w, for the water incorporation reaction, eq 2, can be written, assuming ideal solution behavior, as

$$K_w = \frac{[OH_O^\bullet]^2}{P_{H_2O}[V_O^{\bullet\bullet}][O_O^\times]} \tag{3}$$

where $[OH_O^\bullet]$ and $[V_O^{\bullet\bullet}]$ are the proton and vacancy concentrations, respectively, $[O_O^\times]$ is the concentration of oxygen

ions on normal oxygen sites, and P_{H_2O} is the water partial pressure. The equilibrium constant, K_w, can further be expressed in terms of the entropy, ΔS_W, and the enthalpy, ΔH_W, of the water incorporation reaction

$$K_w = \exp\left(\frac{\Delta S_w}{R}\right)\exp\left(-\frac{\Delta H_w}{RT}\right) \tag{4}$$

where T is temperature and R is the universal gas constant. Even taking $[OH_O^\bullet]$ to be known from the TGA data, it is not possible to directly evaluate K_w on the basis of eq 3 because $[V_O^{\bullet\bullet}]$ and $[O_O^\times]$ are unknown quantities. Thus, a more complete treatment of the defect chemistry is required.

In addition to ionic defects, electronic defects, in particular holes, can also occur in barium zirconate. Under moderately to highly oxidizing conditions, acceptor-doped perovskites can be oxidized in a process that consumes oxygen vacancies and produces electronic holes.[8,19]

$$1/2O_2 + V_O^{\bullet\bullet} \leftrightarrow O_O^\times + 2h^\bullet \tag{5}$$
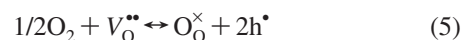
In principle, under reducing conditions, an analogous reaction to eq 5 in which excess electrons are generated should also be considered. Under the experimental conditions explored in this work, however, the electron concentration is negligible (more highly reducing conditions are necessary to generate such defects[8,20,21]), and the reduction reaction is not treated. On consideration of eq 5, it is apparent that if oxidation of the material occurs to any significant extent, the change in sample weight will reflect changes in the oxygen content, $[O_O^\times]$, as well as changes in water content. Thus, while eqs 3 and 4 still apply, the hydroxyl concentration, $[OH_O^\bullet]$, is not uniquely specified by the TGA measurements. Ignoring this inconsistency for the moment, it is nevertheless possible to continue with the defect chemical analysis.

Given the set of defects described in reactions 1, 2, and 5, the overall electroneutrality condition is given as

$$2[V_O^{\bullet\bullet}] + [OH_O^\bullet] + p = [Y_{Zr}'] \tag{6}$$

where $[Y_{Zr}']$ is the concentration of yttrium positioned on zirconium sites. Furthermore, the number of oxygen sites per formula unit of barium zirconate is restricted to 3, implying the site restriction relationship

$$[V_O^{\bullet\bullet}] + [O_O^\times] + [OH_O^\bullet] = 3 \tag{7}$$

With these relationships (specifically, eqs 3, 6, and 7), the equilibrium constant for the water incorporation reaction can be reformulated as

$$K_w = \frac{4[OH_O^\bullet]^2}{P_{H_2O}(6 - [Y_{Zr}'] - [OH_O^\bullet] - p)([Y_{Zr}'] - [OH_O^\bullet] - p)} \tag{8}$$

To permit evaluation of K_w, it is common practice to assume that the unknown hole concentration, p, is negligible, giving the expression

$$K_w^{p=0} = \frac{4[OH_O^\bullet]^2}{P_{H_2O}(6 - [Y_{Zr}'] - [OH_O^\bullet])([Y_{Zr}'] - [OH_O^\bullet])} \tag{9}$$

Applying the methodology of eq 9 to the TGA data measured here yields the results presented in Figure 6, where $K_w^{p=0}$ is plotted in Arrhenius form. For comparison, values
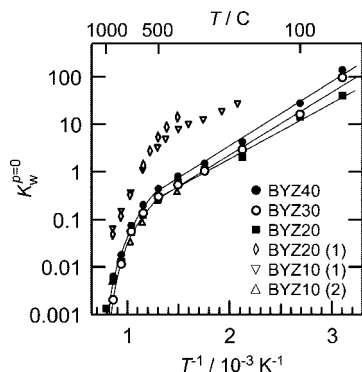
Figure 6. Equilibrium constant for water incorporation reaction calculated in BYZ20−40 using eq 9 by neglecting hole concentration. The equilibrium constants calculated by the same methodology using raw data of (1) Kreuer et al.[12] and (2) Schober and Bohn[11] are also shown.

computed by an identical manner for BYZ10 using the raw proton concentration data of Kreuer[12] and of Schober and Bohn[11] are also shown in the figure. At low temperatures, where the hole concentration is expected to be negligible and weight changes are entirely due to hydration, $K_w^{p=0}$ is, indeed, linear in the Arrhenius representation. At higher temperatures (above ~500 °C), however, the behavior deviates substantially from linearity, displaying a sharp increase in slope. In principle, this deviation may result from temperature dependences of the entropies and enthalpies of water incorporation, but more plausible are the influences of nonnegligible hole concentrations and changes in oxygen content at high temperatures.[8,19−21]

The deviation from linearity is clearly evident in both sets of literature results, as well as the new results obtained here (Figure 6). In Kreuer's data, a change in slope occurs around 450 °C, which is entirely consistent with what is observed in the present study. The overall higher $K_w^{p=0}$ values (obtained from Kreuer's work) are simply a reflection of the overall higher water uptake measured by those authors. Turning to the results of Schober and Bohn,[11] although their study was limited to high temperatures, the computed $K_w^{p=0}$ are comparable to those determined for BYZ20 in the present study. The consistent behavior of $K_w^{p=0}$, as measured in three different laboratories, strongly suggests that the significant deviation from linearity at temperatures above ~500 °C is not an experimental artifact but rather a physical reality. The authors of the previous studies utilized $K_w^{p=0}$ values computed at high temperatures, in the range of about 500−900 °C, to extract hydration entropies and enthalpies. Values on the order of −87 to −103 J K^{-1} mol^{-1} for the former and −74 to −94 kJ mol^{-1} for the latter were reported. Performing a similar analysis here would imply comparable entropy and enthalpy values (~−100 J K^{-1} mol^{-1} and ~−70 kJ mol^{-1}, respectively), not unexpected, given the similarity in the general features of the data sets in Figure 6.

Given the challenges of applying eq 9 at high temperatures, we propose that more meaningful values of the thermodynamic parameters for hydration are obtained from analyses restricted to low temperatures at which $K_w^{p=0}$ behaves linearly on the Arrhenius plot. Specifically, we select the range 50−500 °C, and not surprisingly, the resulting hydration enthalpies and entropies (−22 to −26 kJ mol^{-1} and −39 to −44 J K^{-1} mol^{-1}, respectively) are smaller in magnitude than those reported in the literature.

A comprehensive comparison with literature results is presented in Table 1, in which the thermodynamic data for barium zirconate,[11,12] strontium zirconate,[22,25] barium cerate,[23] strontium cerate,[24,26] and strontium titanate[12,27] are summarized, along with the experimental conditions under which the TGA data were collected. For all but strontium titanate (as reported by Kreuer et al.), measurement temperatures were between 400 and 1100 °C, and hydration enthalpies fall in the range −60 to −157 kJ mol^{-1}. The anomalous result for strontium titanate is significant in that the analysis was limited to a low temperature regime, and the hydration enthalpy corresponds closely to the present results. Despite the differing experimental conditions for evaluation of K_w, it is noteworthy that the hydration thermodynamics are independent of dopant concentration in both the earlier and present studies of doped barium zirconate.

Returning to the question of possible incomplete equilibration at low temperatures in the present TGA experiments, it is of value to consider the impact of a 2−7% error in proton content on the derived thermodynamic parameters. Recalculation of K_w using the extrapolated weight values (assuming a stretched exponential relaxation process, as discussed above) results in entropy and enthalpy values (−42 J K^{-1} mol^{-1} and −27 kJ mol^{-1}, respectively, in BYZ40, for example) that are statistically equivalent to the ones originally obtained. Thus, the slight uncertainty in the proton concentration at low temperatures does not meaningfully affect a discussion of the thermodynamic parameters.

Some physical insight into the significance of the thermodynamic parameters obtained for BYZ can be gained from a comparison with the characteristics of hydrogen dissolution into metals. Similar to water uptake in oxides, hydrogen uptake in metals is characterized by the entropy Δs_s and the enthalpy Δh_s of hydrogen dissolution (typically expressed for the dissolution of one mole of hydrogen atoms rather than H$_2$ molecules). The experimental values of Δh_s span a wide range, from −91 to 106 kJ mol^{-1},[28] and are largely determined by the gross electronic structure of the host metal. Macroscopically, Δh_s is a measure of the tendency toward compound (hydride) formation. The values of ΔH_w, obtained here for BYZ, −22 to −26 kJ mol^{-1}, are small in magnitude relative to typical values of $2\Delta h_s$, suggesting rather weak chemical binding between the dissolved hydroxyl group and the host oxide. Even in the group 5 elements V, Nb and Ta,

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Table 1. Hydration Enthalpies and Entropies Determined in Proton Conducting Oxides in Terms of Thermogravimetry[a]

materials	dopant content	temp range[b]/°C	water vapor pressure/atm	hydration enthalpy/ kJ mol⁻¹	hydration entropy/ J K⁻¹ mol⁻¹	year	authors	ref
barium zirconate	20% Y	50−500	0.023	−22 ± 1	−39 ± 1	2008	this work	
	30% Y	50−500	0.023	−26 ± 1	−44 ± 1	2008	this work	
	40% Y	50−500	0.023	−26 ± 1	−41 ± 1	2008	this work	
	10% Y	500−800	0.005−0.04	−74 ± 3	−87 ± 10	2000	Schober and Bohn	11
	2% Y	∼600−∼800	0.023	−80.9	−94.4	2001	Kreuer et al.	12
	5% Y	∼500−∼800	0.023	−79.5	−93.5	2001	Kreuer et al.	12
	10% Y	∼500−∼900	0.023	−79.4	−88.8	2001	Kreuer et al.	12
	15% Y	∼500−∼900	0.023	−83.4	−92.1	2001	Kreuer et al.	12
	20% Y	∼550−∼900	0.023	−93.3	−103.2	2001	Kreuer et al.	12
	10% Sc	∼500−∼900	0.023	−119.4	−124.9	2001	Kreuer et al.	12
	10% Gd	∼600−∼900	0.023	−66.1	−85.9	2001	Kreuer et al.	12
	10% In	∼450−∼900	0.023	−66.6	−90.2	2001	Kreuer et al.	12
strontium zirconate	5% Yb	400−900	0.005−0.04	−106	−127	1997	Krug and Schober	22
	10% Y	500−900	0.005−0.04	−125	−151	2001	Schober	25
barium cerate	19% Y	∼500−∼850	∼0.001−∼0.035	−158	−172	1996	Kreuer et al.	23
strontium cerate	5% Eu	600−800		−164		2003	Song et al.	26
strontium titanate	2% Sc	∼230−∼440	1	−22.9	−99.5	2001	Kreuer et al.	12
	1% Fe	400−600	0.004−0.1	−60 ± 12	−122 ± 9	2005	Yu et al.	27

[a] The experimental condition is also noted. [b] Temperature range shown is the range where hydration enthalpy has been determined in the experiment.

which preferentially form solid solutions with hydrogen rather than hydride compounds, the values are −54, −68, and −75 kJ mol⁻¹, respectively.[28] Turning to the entropy of dissolution, by far, the major contribution to this term, for the case of hydrogen dissolution into metals, derives from the loss of the entropy of the gas phase. At $T = 25$ °C and $p = 0.1$ MPa, the specific molar entropy of $H_2(g)$ is 130.7 J K⁻¹ mol⁻¹,[29] implying a Δs_s of approximately −65.4 J K⁻¹ mol⁻¹. The experimental values of Δs_s range from −33 to −75 J K⁻¹ mol⁻¹, indicating that, indeed, other factors are generally small contributors to the entropy change.[28] For oxide hydration, the analogous relevant quantity, the specific molar entropy of $H_2O(g)$, is 188.8 J K⁻¹ mol⁻¹.[29] The experimental values of $-\Delta S_w$ obtained for BYZ in this work (∼40 J K⁻¹ mol⁻¹) are thus substantially smaller than what would be expected for the complete loss of entropy on dissolution, implying that substantial entropy is introduced into the oxide as a consequence of the hydration. Heat capacity measurements may serve to further elucidate these characteristics.

In closing, it is valuable to consider whether one can utilize the $K_w^{p=0}$ determined from the low temperature measurements, which presumably corresponds to K_w for all temperatures, and extract from the high-temperature nonlinearity of $K_w^{p=0}$ on the Arrhenius plot characteristics of the oxidation reaction. Such an analysis appears impossible because it is not possible from the TGA data alone to distinguish between weight changes due to oxidation and those due to hydration.

Independent measurements of the oxidation behavior (e.g., thermal analysis under dry O_2 conditions) are required for a complete thermodynamic analysis of BYZ, and such measurements are under way.

5. Conclusions

Thermogravimetric analysis has been carried out in yttrium-doped barium zirconate with a 20−40% yttrium concentration in the temperature range from 50 to 1000 °C under humidified nitrogen with a water partial pressure of 0.023 atm. The proton concentration in BYZ gradually decreases with increasing temperature, whereas it increases with increasing yttrium content. The equilibrium constants for the water incorporation reaction, calculated under the assumption of negligible hole concentrations, show linear behavior in the Arrhenius representation over the temperature range from 50 to 500 °C, whereas at higher temperatures, the behavior deviates substantially from linearity. The hydration enthalpies evaluated at the low temperature range are −22, −26, and −26 kJ mol⁻¹ in BYZ20, -30, and -40, respectively. The smaller negative values in comparison with the literature are attributed to the restriction of the analysis to the low temperatures at which electronic hole concentrations can be neglected. The hydration entropies in BYZ, around −40 J K⁻¹ mol⁻¹, are substantially smaller than what would be expected for the complete loss of entropy of water vapor dissolution.

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