

# Hydrogen content in doped and undoped BaPrO<sub>3</sub> and BaCeO<sub>3</sub> by cold neutron prompt-gamma activation analysis

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Proton uptake in undoped and Y-doped BaPrO<sub>3</sub> has been measured by cold neutron prompt-gamma activation analysis, and compared to the proton uptake in Gd-doped BaCeO<sub>3</sub>, as determined by the same technique. The conventional proton incorporation model of perovskites in which oxygen ion vacancies, generated by the introduction of the trivalent dopant onto the tetravalent perovskite site, are filled with hydroxyl groups upon exposure of the sample to H<sub>2</sub>O containing atmospheres, predicts that the proton concentration in such materials should be no greater than the dopant concentration. In contradiction to this model, the proton concentration in BaPr<sub>1-x</sub>Y<sub>x</sub>O<sub>3</sub> after humidification is as much as three times greater than the dopant concentration, and even undoped samples contain a high concentration of protons. Moreover, x-ray photoemission spectra suggest that the Pr oxidation state is lowered upon hydration. In contrast, BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub> shows a typical hydrogen concentration, of close to 90% of the yttrium concentration. The results are interpreted in terms of the variable valence of Pr, which can become reduced from the 4<sup>+</sup> to the 3<sup>+</sup> oxidation state upon exposure to water, and effectively behaves as a self-dopant within the structure. © 2005 American Institute of Physics. [DOI: 10.1063/1.1922590]

## INTRODUCTION

Many doped perovskite oxides including BaCeO<sub>3</sub>, BaZrO<sub>3</sub>, SrCeO<sub>3</sub>, and SrZrO<sub>3</sub> have received recent attention as proton conductors.<sup>1</sup> Introduction of a trivalent dopant onto the quadravalent site results in the creation of oxygen vacancies. Upon exposure of the material to humid atmospheres OH groups are dissolved onto the formerly vacant oxygen sites and additional protons are incorporated at other oxygen ion sites. Protons, present in the form of hydroxyl ions, can easily jump from one oxygen ion to the next, giving rise to the observed high proton conductivity. To date, few mixed proton and electron conducting oxides, as would be useful in a variety of applications, have been examined. As part of an ongoing program to develop such materials, we have examined the properties of BaPrO<sub>3</sub>. In analogy to compounds such as SrCeO<sub>3</sub> and BaCeO<sub>3</sub>, acceptor-doped BaPrO<sub>3</sub> might be anticipated to adsorb atmospheric H<sub>2</sub>O and exhibit good proton conductivity, whereas the variable valence of the Pr ion, between the 3<sup>+</sup> and 4<sup>+</sup> oxidation states, might be anticipated to produce high electronic conductivity. Although there is some disagreement as to the relative contributions of protonic and electronic conductivity in doped BaPrO<sub>3</sub>, indeed both means of charge transport appear to occur.<sup>2,3</sup> In addition, BaPrO<sub>3</sub> is unusual in its ability to host Pr primarily (if not entirely) in the 4<sup>+</sup> oxidation state, and has therefore been of interest for its magnetic properties.<sup>4-9</sup>

Measurement of hydrogen (or water) uptake in proton conducting perovskites has typically been carried out by

thermogravimetric methods,<sup>1</sup> although in a limited number of cases other techniques have been employed. In an early example, the water solubility in yttria-stabilized zirconia (YSZ) has been determined from a measurement of the equilibrium water vapor pressure above the material,<sup>10</sup> whereas measurement of the integrated OH stretching band as determined from IR spectroscopy has been somewhat more recently employed in the case of strontium titanate.<sup>11</sup> In another example, SIMS (second-ion-mass spectroscopy) has been utilized for examining selected fluorite and perovskite oxides.<sup>12</sup> For a compound such as BaPrO<sub>3</sub>, thermogravimetric methods are inappropriate because of the potential for Pr reduction and therefore weight change due to oxygen loss. In addition, for all alkaline-earth perovskites care must be taken to eliminate the influence of surface carbonates on the weight change measurement due to the loss of CO<sub>2</sub> at high temperatures. In this work, we have employed cold neutron prompt-gamma activation analysis (PGAA) to precisely determine the hydrogen content in undoped and doped BaPrO<sub>3</sub>. This nondestructive technique involves exposure of a material to a neutron beam which induces neutron capture and concomitant gamma radiation release. The energy of the gamma rays depends on the element (or, more specifically, the isotope) undergoing the transformation whereas the number of gamma rays is directly proportional to the element concentration. PGAA has the advantage of yielding accurate stoichiometries over a very wide compositional range, so long as a calibration between gamma ray count and concentration is established, and energy overlap between different elements in the sample is not severe. The method is particularly sensitive for hydrogen, for which detection limits in the parts

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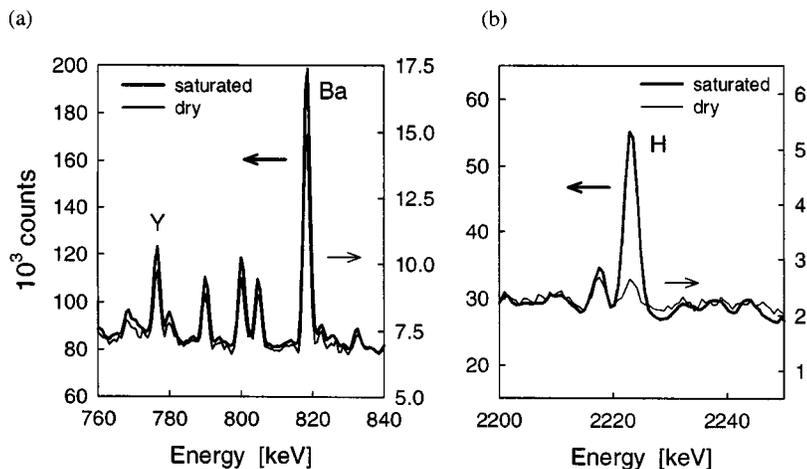


FIG. 1. PGAA spectra of the saturated and dry  $\text{BaPr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$  in selected energy regions; (a) sensitivity to Y and Ba; (b) sensitivity to H and the effect of  $\text{H}_2\text{O}$  saturation.

per million can be achieved with sufficiently large samples and adequate counting times. It has been profitably employed to measure the proton concentration in the related compound,  $\text{SrCeO}_3$ .<sup>13</sup>

## EXPERIMENT

Samples of  $\text{BaPr}_{1-x}\text{Y}_x\text{O}_{3-\delta}$  (with  $x=0, 0.1, 0.15$ , and  $0.2$ ) were prepared by conventional solid-state reaction using  $\text{BaCO}_3$  (99.95%),  $\text{Pr}_6\text{O}_{11}$  (99.9%), and  $\text{Y}_2\text{O}_3$  (99.9%) as the starting materials. Prior to use,  $\text{BaCO}_3$  was held at  $500^\circ\text{C}$  for 2 h so as to remove any water absorbed on the surface. After ball milling for 48 h, the mixtures were calcined at  $800^\circ\text{C}$  for 5 h,  $1000^\circ\text{C}$  for 10 h, and  $1350^\circ\text{C}$  for 12 h in air with intermediate grindings. Samples were examined in both dry and hydrated conditions, where hydration was achieved by exposing the samples to water-saturated argon ( $P_{\text{H}_2\text{O}}=0.03$  atm) at  $400$ – $500^\circ\text{C}$  for several hours. In addition, hydrated  $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_3$  was also prepared in an analogous fashion.<sup>14</sup> The cerate, for which  $\text{H}_2\text{O}$  content is well established, was used to provide a check of the measurements.

For the PGAA measurements, samples (0.1–0.4 g in mass) were sealed in envelopes ( $4 \times 4$  cm<sup>2</sup>) of Teflon film under ambient conditions. Data were collected on the neutron guide NG-7 (Ref. 15) at the NIST Center for Neutron Research (at room temperature). The neutron beam was collimated to a 2-cm diameter with a  $^6\text{Li}$  glass aperture. The sample envelopes were mounted vertically on the instrument such that the beam irradiated an area near the center of the sample. Prompt-gamma emissions were detected with a high-purity  $n$ -type germanium detector (Cannberra),<sup>15</sup> with a relative efficiency of 35% and a resolution of 1.75 keV [full width at half maximum (FWHM)] at 1.33 MeV. The detector is connected to a 16 384-channel pulse-height analyzer with an energy range of 80–11 000 keV. Compton suppression was employed during some of the measurements. Some slight variations in the gamma-ray energies (1 keV or less) occurred due to the drift in the detector electronics and other intrinsic instrumental factors. To correct for this drift, standards were measured along with the samples. For H, Y, and Ba, the standards were  $\text{CO}(\text{NH}_2)_2$  (urea),  $\text{Y}_2\text{O}_3$ , and  $\text{BaF}_2$ , respectively. A background spectrum from an empty Teflon envelope was also measured. The sample chamber was

evacuated during the measurements. Irradiation times were varied, depending primarily on the size of the sample, in order to achieve a relative error of approximately 1% from counting statistics on the integrated intensities of the emission lines of interest. Selected samples were measured twice (in different beam cycles) to ensure the reproducibility of the results. The elemental ratios H:Ba and H:Y were calculated rather than absolute amounts of the elements, in order to avoid any analytical bias.<sup>16</sup>

The chemical analysis was additionally complemented by x-ray photoemission spectroscopy (XPS) studies in order to provide a measure of the Pr oxidation state. Data were collected from both the dry and hydrated samples using an M-probe surface spectrometer (VG Instruments). Monochromatic  $\text{Al K}\alpha$  x-rays (1486.6 eV) incident at  $35^\circ$  from the horizontal were used to excite electrons from the sample, and the emitted electrons collected by a hemispherical analyzer. To prevent charging of the powder during data collection, the sample was flooded from above with low-energy ( $<5$  eV) electrons emitted from a hot filament. The data were recorded with a nominal resolution of 1.0 eV, using the data collection software package ESCA Capture E. Repeated measurements carried out for long periods of time ( $>35$  h) showed high reproducibility and no loss in resolution, indicating the absence of artifacts due to charging.

## RESULTS AND DISCUSSION

Examples of typical spectra are shown in Fig. 1, and the extracted chemical compositions of the samples are presented in Table I. In Fig. 2 a plot of the measured H:Ba ratios as a function of dopant concentration is shown. From the results of Fig. 1 it is apparent that the PGAA method is highly sensitive to all the elements of interest, Y, Ba, and H, whereas Fig. 1(b), demonstrates the sensitivity of the technique to proton (hydrogen) incorporation upon hydration. The accuracy of the measurements can be assessed from a comparison between the nominal and measured stoichiometries. The measured barium to yttrium ratios differ from the nominal by amounts of 2%–10%, with the measured value typically being lower than the nominal. Barium loss from barium cerate-based materials upon high-temperature processing has been reported,<sup>17</sup> and a similar phenomenon may

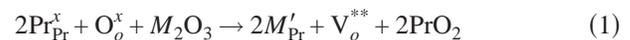
TABLE I. Chemical composition of perovskites as determined by PGAA. For H<sub>2</sub>O-saturated samples, the expected H:Y ratio is 1:1, whereas for dry samples it is 0:1.

Sample	H:Y	Expt.	Ba:Y	Expt.	H:Ba	Expt.
<b>Dry</b>						
BaPrO <sub>3</sub>	N/A	N/A	N/A	N/A	0.0624(22)	0.00
BaPr <sub>0.9</sub> Y <sub>0.1</sub> O <sub>3</sub>	0.74(10)	0	9.2(4)	10	0.081(10)	0.00
Run 1	0.694(96)		9.29(37)		0.0749(99)	
Run 2	0.789(17)		9.133(84)		0.0864(19)	
BaPr <sub>0.8</sub> Y <sub>0.2</sub> O <sub>3</sub>	0.472(11)	0	4.842	5	0.0974	0.00
<b>H<sub>2</sub>O-saturated</b>						
BaPrO <sub>3</sub>	N/A	N/A	N/A	N/A	0.102(4)	0.00
BaPr <sub>0.9</sub> Y <sub>0.1</sub> O <sub>3</sub>	3.07(4)	1.0	9.20(9)	10	0.334(3)	0.10
BaPr <sub>0.85</sub> Y <sub>0.15</sub> O <sub>3</sub>	3.33(14)	1.0	6.65(23)	6.67	0.50(3)	0.15
Run 1	3.24(13)		6.75(22)		0.480(15)	
Run 2	3.436(25)		6.557(59)		0.5240(43)	
BaPr <sub>0.8</sub> Y <sub>0.2</sub> O <sub>3</sub>	1.847(18)	1.0	5.131(37)	5	0.360(3)	0.20
<b>Reference</b>						
BaCe <sub>0.9</sub> Y <sub>0.1</sub> O <sub>3</sub>	0.87(16)	1.0	9.03(22)	10	0.098(18)	0.10
Run 1	0.777(45)		9.07(21)		0.0857(47)	
Run 2	0.998(12)		8.992(73)		0.1110(14)	

occur here as well, however, the relatively low calcination temperature employed in the present study for the synthesis of BaPrO<sub>3</sub>-based compounds suggests the possibility of an inherent systematic error in the composition measurements. The precision of the measurements, as assessed in terms of the reproducibility of the Ba:Y values for samples measured twice, is quite good, with first and second values that are within 3% of one another. In the case of the H:Y or H:Ba ratios, the reproducibility for the two samples containing small proton concentrations (BaPr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub> dry and BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub> saturated) is poorer (differing by as much as 25% between the two runs), and presumably reflects the poorer counting statistics for the weak proton signal from these samples. The estimated standard deviations for each measurement (as determined either from the counting statistics or from the averaging of two measurements) are included in Table I for each result, and it is apparent that, overall, the composition trends observed are reliable. Moreover, for the reference material, hydrated BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub>, the

measured H:Y ratio is  $0.87 \pm 0.16$ , in good agreement with literature values,  $\sim 0.82$ ,<sup>1</sup> and as such further validates the results.

Examination of Fig. 2 reveals a surprising result, specifically, that the H concentration in BaPrO<sub>3</sub>-based materials is significantly higher than the dopant concentration. In contrast, the simple picture of H<sub>2</sub>O incorporation into perovskites, in which oxygen vacancies are generated as a result of trivalent ion doping, Eq. (1), are subsequently filled by hydroxyl groups and a second proton attaches to some other oxygen ion in the structure, Eq. (2), implies that the proton concentration should at most equal that of the dopant concentration:



In the case of hydrated barium cerate these two numbers are indeed comparable, as noted above (with the H concentration being 87% that of the Y concentration). In the case of hydrated BaPr<sub>1-x</sub>Y<sub>x</sub>O<sub>3</sub>, however, the H concentration is as much as five times greater than the Y concentration. Moreover, even nominally dry samples have significant H content.

The XPS spectra, Fig. 3, of BaPrO<sub>3</sub> in the dry and hydrated states show the characteristic features noted in the literature for the praseodymium bearing oxides, PrO<sub>2</sub>,<sup>18</sup> Pr<sub>2</sub>O<sub>3</sub>,<sup>19</sup> BaPrO<sub>3</sub>, and BaPr<sub>2</sub>O<sub>4</sub>.<sup>20</sup> In particular, a spin-orbit-splitting energy of  $\sim 20$  eV between the Pr 3d<sub>5/2</sub> and the Pr 3d<sub>3/2</sub> lines is apparent, and the overall spectrum is comprised of three pairs of peaks. The changes in the electron state responsible for each of these pairs of peaks has been presented by Ogasawara *et al.*<sup>19</sup> and discussed further by Felner *et al.*<sup>20</sup> What is relevant for this work is the shift in the peaks towards lower binding energies upon hydration (most evident for the B-B' pair of peaks which shift by about 0.07 eV), as well as a reduction in the intensity of the A-A' pair of

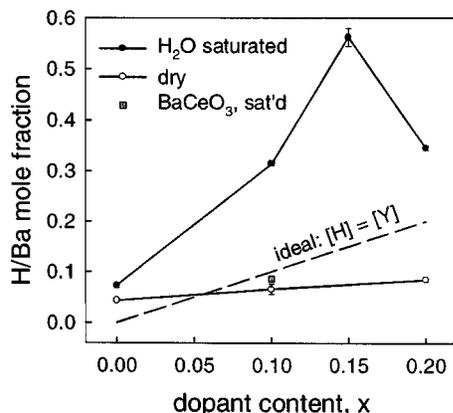


FIG. 2. Hydrogen concentration in saturated and dry BaPr<sub>1-x</sub>Y<sub>x</sub>O<sub>3-δ</sub> as measured by PGAA and comparison with saturated BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub>.

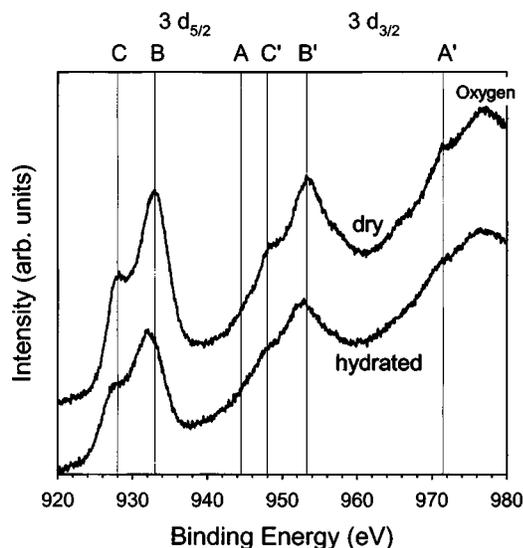
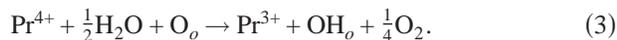


FIG. 3. Comparison of the x-ray photoemission spectra obtained from BaPrO<sub>3</sub> in the dry and hydrated states. Peak labels correspond to those given in Ref. 18.

peaks. From a comparison with the spectra reported for BaPrO<sub>3</sub> and BaPr<sub>2</sub>O<sub>4</sub>,<sup>20</sup> these changes are consistent with an overall decrease in the Pr oxidation state.

In light of the XPS results, we attribute the unusually high hydrogen content in BaPrO<sub>3</sub> to the variable valence of Pr, which can become reduced from Pr<sup>4+</sup> to Pr<sup>3+</sup> upon exposure to H<sub>2</sub>O. Essentially, the compound can “self-dope” with the effective M<sup>3+</sup> dopant concentration being much greater than the amount of Y<sup>3+</sup> introduced during synthesis. Overall, the reaction can be written as



Thus, the change in the oxidation state of Pr is accompanied by the release of oxygen from water molecules. This mechanism apparently outweighs proton incorporation via reactions (1) and (2), and as much as ~30% of the Pr ions must change oxidation state in order to account for the large proton concentrations measured.

An alternative possibility is that the proton signal measured by the PGAA method reflects water adsorbed onto the surface of the BaPrO<sub>3</sub> particles. However, the quantity of water that could be realistically accounted for in this way is far smaller than that implied by the measured PGAA signal. The powders examined here have a particle size of ~1 μm, and assuming that a monolayer of water is adsorbed onto the particle surface, the H/Ba ratio would be only on the order of

$1.5 \times 10^{-3}$ . Additional qualitative evidence supporting the proposed interpretation [i.e., proton incorporation via Eq. (3)] derives from a nominally unrelated set of experiments in which quantitative analysis of the Pr oxidation state in BaPrO<sub>3</sub> was attempted by chemical titration methods.<sup>21</sup> There, it was noted that upon dissolution of BaPrO<sub>3</sub> into acidic media, oxygen evolution indeed occurred due to Pr<sup>4+</sup> oxidation of water.

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