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Abstract

We have successfully demonstrated high rates of proton, deuterium and tritium ion transport in (Sr,Ba)(Zr,Ce)(B)³⁺O_{3-y} perovskite structure oxides at high temperatures. AC impedance studies of the isotope effect upon transport properties indicate that the conduction mechanism involves the hopping of a hydrogen isotope ion from octahedral oxygen sites. The hydrogen isotope ion does not involve the motion of a hydrated ion in the conduction process. This is in sharp contrast to low temperature proton conducting solids. The conductivity is highest for protons followed by deuterons then tritons. The activation energies for conduction are approximately 0.60 eV for all isotopes. Carrier concentrations were also invariant with isotope mass for similar doping levels. Variation in the conductivity was therefore due to differences in phonon frequencies between OH, OD and OT species. The perovskite oxides were shown to be structurally stable to high levels of tritium beta decay radiation.

Background and Research Objectives

Commensurate with the end of nuclear weapons production and the initiation of the DOE Stockpile Stewardship policies arises the difficult task of the recovery of tritium and tritiated species from impurities such as water and hydrocarbons. Aside from the need for environmental clean-up and waste mitigation, the decommissioning of reactors for tritium production places emphasis on tritium recycling.

The current state-of-the-art for tritium recovery utilizes a palladium membrane reactor (PMR) which is a combined reactor/permeator. The decomposition of tritiated water and hydrocarbons is carried out using "shift" reaction chemistry on a Pt catalyst; the hydrogen product from these reactions is removed using an evacuated Pd/Ag tube which is only permeable to hydrogen isotopes. The removal of hydrogen then facilitates further shift reactions. This technology is being developed at the Tritium System Test Assembly at Los Alamos and has achieved hydrogen recovery factors on the order of 10⁸. This separation factor is a significant improvement over existing technologies given the simple hardware requirements and the desire for once-through processing without the generation of additional tritiated waste.

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However, aside from the significant expense of Pd (\$6500/kg), the hydrogen pressure difference that drives the diffusion process across the separator is limited by the vacuum that can be obtained using ULV technology (10^{-8} to 10^{-9} torr). We have investigated the materials feasibility of tritium recovery using solid state electrochemical pumping cells based on proton ion conducting solid electrolytes (Fig 1). Unlike the transport of neutral hydrogen in the permeation process, these ceramic materials will transport hydrogen ions through the crystalline lattice. These materials offer a number of potential advantages over vacuum pumping systems:

1. Electrochemical ion pumping cells do not rely on physically induced pressure differences for separation and can achieve separation factors many orders of magnitude greater than with vacuum technology. For example, electrochemical oxygen pumping cells that utilize Y-ZrO₂ oxygen ion conductors can routinely reduce oxygen partial pressures to 10^{-20} at 800°C. Analogous to oxygen ion-conducting oxides are a class of oxides that conduct protons at temperatures below 900°C. Like oxygen ion conductors, these materials have received widespread attention in recent years for their potential use in solid oxide fuel cells
2. The ceramic ion pumps are solid state devices with no moving parts to malfunction and they operate at ambient pressure.
3. These ceramic cells operate at the temperatures required to catalyze the gas shift reactions and therefore, they do not need to be cooled or physically isolated from the shift reactor.
4. Unlike polymer membrane electrolytes, the ceramic materials should be far more stable in high beta radiation environments. The ionic bonding and elevated operating temperatures should make the system "self annealing" to radiation damage.

We anticipate additional advantages from our approach. In addition to electrochemical enhancement and control of the shift reaction chemistry, the rate of electrochemical pumping of hydrogen isotopes through a solid oxide is governed by the diffusion coefficient of the diffusing species. Thus techniques such as pulsed ion chromatography and electrophoresis where a time varying potential is applied across a proton conductor of a specific diffusion path length may be utilized for hydrogen isotope separation.

Importance to LANL's Science and Technology Base and National R&D Needs

Techniques for the recovery of tritium gas and removal of tritium from hydrocarbon gases are crucial in order to maintain this nation's nuclear stockpile and are at the heart of this laboratory's core technical competencies of stockpile support and stewardship and nuclear materials management. In addition, the recovery of tritium from the amassed mixed waste in the nuclear weapons complex is also of great national importance and this work is therefore applicable to Environmental Stewardship as well.

There presently exists about two tons of tritiated water at Mound, LANL and Savannah River Site. This presents a formidable processing challenge. While present PMR technology is capable of processing this material an improved membrane would make this processing less daunting. New technologies such as the one presented here that combine high separation rates, and reduced costs, complexity and size are welcome enhancements to meet processing demands. The work performed here provides the data necessary to determine whether the promising technology presented here can form the basis for such an enhancement which would reduce processing, installation, and operating costs.

Ammonia, ammonia based fertilizers, and sulfuric acid represent the largest weight percentage of chemicals produced in the world. High flow rate hydrogen separation technology will be an important defense spin-off to the hydrogen-based chemical industries. To make these applications practical, high flux, low cost hydrogen separators are key to reducing production costs while increasing product yield and reducing waste.

Scientific Approach and Accomplishments

The general objective of our work is the evaluation of perovskite oxide materials suitability for hydrogen isotope separation applications. High temperature proton conductive ceramics based on SrCeO_3 , BaCeO_3 , CaZrO_3 , and SrZrO_3 were first reported by Iwahara [1]. Substitution of the cerium or zirconium tetravalent cation for a trivalent cation, typically yttrium or a rare earth element, yields a vacant oxygen site. Water vapor will hydrolyze on these vacant sites to fill the vacancy with an oxygen atom and provide two mobile interstitial protons. Since the first reports, Iwahara and other investigators have studied the conductivities (both ionic and electronic), conduction mechanism, deuterium isotope effect, and thermodynamic stability of these materials.

The motivation for most of this work derives from the desire to utilize these materials for high temperature, hydrogen-fueled solid oxide fuel cells. In a reverse operation mode, if metal or metal oxide electrodes are deposited onto a dense pellet of this material and is heated to temperature T, the application of an electric potential to the electrodes will cause a hydrogen partial pressure difference across the pellet according to the Nernst equation:

$$\Delta V = -\frac{RT}{zF} \ln \frac{P_{H_2}}{P_{H_2}}$$

where F is Faraday's constant and z is the number of electrons transferred upon oxidation and reduction. For example, at 500°C the application of 1.5V would produce a hydrogen partial pressure difference across a pellet on the order of 10^{20} .

Although a H/D isotope effect has been shown in proton-conducting perovskites, the data in the literature is neither extensive nor consistent enough to clearly establish a model for the tritonic conduction in these perovskites [2]. The measured difference in activation energies for the H and D-ion conduction has eliminated the possibility of proton hopping governed by a classical theory and has given support to a semi-classical approach. This approach takes into consideration the difference in zero point energies between the ground state of H and D, given by the following equation:

$$E_D - E_H = \frac{1}{2} h(\nu_D - \nu_H) \quad (1)$$

where E_H and E_D are the activation energies for the H and D-ion conduction respectively and ν_H and ν_D are the OH and OD stretching frequencies. However the pre-exponential factors presented in the literature do not obey the predictions of the semi-classical theory given by [3]:

$$A_{H/D/T} = z\lambda^2 e^2 \nu_{H/D/T} c_{\text{eff}} / 6vk \text{ and } A_H/A_D = \sqrt{2} \text{ and } A_H/A_T = \sqrt{3} \quad (2)$$

Where $z = 8$ (number of jump directions), $\lambda =$ jump distance (O-O distance), $c_{\text{eff}} =$ concentration of mobile protons, and $v =$ unit cell volume.

Our goal of this research study was the measurement of the H, D and T-ion conductivities of $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ and $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$, and the determination of the validity of this model for tritonic conductivity.

Single phase perovskite samples of $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$, $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ and $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ were prepared using standard solid state methods by heating appropriate stoichiometric mixtures of BaCO_3 , SrCO_3 , CeO_2 , ZrO_2 and Yb_2O_3 at 1773K for 20 hours with two intermediate ball milling steps. The formation of a single-phase orthorhombic perovskite was confirmed by powder x-ray diffraction using a Siemens D 5000 Diffractometer. Dense ceramic samples (typically $\geq 95\%$ theoretical) were obtained by isostatically pressing the powders into pellets at 35 MPa for 5 minutes, and sintering at 1923K for 10 hours. Samples were then cut out of these pellets for TGA and conductivity measurements.

The thermo-gravimetric analysis was performed using a Perkin Elmer TGA 7 Analyzer. The sintered samples were first treated in either "2% H_2 /3% H_2O /Argon" or "2% D_2 /3% D_2O /Argon" gas mixtures at 600°C for 24 hours and furnace cooled to room temperature. This treatment leads to the incorporation of protons or deuterons into the sample. The protonated (deuterated) samples were then heat treated at 1000°C for 16 hours in Ultra high purity argon and the weight loss was monitored.

For the AC impedance measurements, the samples were painted with porous platinum ink on two sides and loaded onto an alumina holder with Pt leads. The measurements were performed using a Solartron 1260 Impedance Analyzer, in the frequency range from 10mHz to 13MHz. For the tritium measurements, the sample along with the holder was sealed in a quartz tube and the setup was kept in a glove box for secondary containment. The tritium level in the glove box was continuously monitored to check for any tritium leaks. The setup was then heated to 600°C under vacuum and the primary containment was leak checked. A "2% T_2 /Argon" -40 curies liter! - gas mixture, 0.76 atm., atmospheric pressure at Los Alamos, was introduced into the setup which was then isolated from the tritium supply. The conductivity was monitored every half-hour for a total of six hours to confirm the tritium incorporation into the sample. The sample was then cooled to room temperature and conductivity measurements were performed every 50°C, from 50°C to 350°C. This procedure was followed in order to minimize and contain the amount of tritium used in the experiment. However, for the H_2 and D_2 measurements the samples were heat-treated in "2% H_2 /3% H_2O /Argon" or "2% D_2 /3% D_2O /Argon" gas mixtures respectively, at 600°C for 24 hours and then furnace cooled to room temperature. Moreover, the H_2 and D_2 conductivity measurements were performed in the flowing gas mixture in the temperature range from 50-350°C.

Results

The TGA results listed in Table 1. indicated that the concentration of protons and deuterons are identical under the treatment conditions used. The maximum proton occupancy was observed for the barium cerate sample (40%) and the minimum for strontium cerate (20%). This observation is consistent with the fact that the barium cerate sample has the highest magnitude of protonic conductivity whereas the strontium cerate has the lowest conductivity. This is also reflective of the fact that the strontium cerate has only 5% Yb dopant and hence only 2.5% oxygen vacancies that can incorporate protons in the wet state.

The total conductivity of these materials consists of a bulk (lattice conductivity) and a grain-boundary contribution. However, for the strontium cerate sample there is a significant overlap in the bulk and grain boundary conductivities as shown in Fig. 2. Using Boukamp-University of Twente's "EQUIVCRT" software, two distinct arcs could be fitted to this data. However, when the protonic conductivity of three different samples were thus analyzed, the scatter in the data was large; for example, $0.57 < \Delta H_H < 0.63$, and $700 < A_H < 3000$. Although this scatter in activation energy values makes it difficult to determine an isotope effect, it is consistent with that reported in the literature[4], where $0.55\text{eV} < \Delta H_H < 0.63$.

This large scatter in activation energy (± 0.06 eV), both in our data and in that available in the literature is primarily due to two factors. The first factor is the variation of proton concentration with changing temperature and the second is the contribution of the grain boundary conductivity. While the first factor is predominant at elevated temperatures ($> 600^\circ\text{C}$) where the concentration of protons in the sample tends to decrease due to water evolution from the sample; the second factor is predominant at the lower temperature regime ($< 600^\circ\text{C}$) where the grain boundary conductivity is significant.

The bulk (lattice) isotope conductivities of $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ and $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ are plotted in Fig. 3 a & b. along with the fitted values of activation energies and pre-exponential factors. The tritium conductivity data which have been reported for the first time in the literature, confirm the increasing activation energy with increasing isotope mass for the $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ sample ($\Delta H_H = 0.56\text{eV}$, $\Delta H_D = 0.58\text{eV}$, $\Delta H_T = 0.61\text{eV}$).

However, for the $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ sample, the change in ΔH between the D_2 and T_2 measurements is within the experimental error ($\Delta H_{\text{H}} = 0.55\text{eV}$, $\Delta H_{\text{D}} = 0.57\text{eV}$, $\Delta H_{\text{T}} = 0.56\text{eV}$). This could be due to the lower concentration of T_2 in the sample and hence some interference due to p-type conductivity which is known to be high in barium cerates. This problem can be mitigated by the incorporation of tritium using " $\text{T}_2/\text{T}_2\text{O}/\text{Argon}$ " mixtures instead of " T_2/Argon " mixtures. However, this experiment was not attempted due to the high risk (human radiological hazard) involved in using tritiated water.

From Fig 3 a & b. it can also be seen that the pre-exponential factor decreases with increasing isotope mass. Moreover, the ratios of $A_{\text{H}}/A_{\text{D}}$ (1.65 and 1.4) and $A_{\text{H}}/A_{\text{T}}$ (2.45 and 2.55) are consistent with the semi-classical theory and within experimental error, close to $\sqrt{2}$ and $\sqrt{3}$ respectively. The larger than $\sqrt{3}$ ratio observed for $A_{\text{H}}/A_{\text{T}}$, could be a result of a lower concentration of tritium incorporated into the sample. However, given the high uncertainty (50%) in the ratios of the pre-exponential factor, it would be more instructive to fit the observed values of $A_{\text{H/D/T}}$ to equation 2 in order to confirm the mechanism of proton migration in these perovskites.

The Sr and Ba-doped cerate electrolytes exhibit the highest proton conductivities, however, recent reports question the thermodynamic stabilities of these compounds at intermediate temperatures and in the presence of high partial pressures of CO_2 and H_2O . We have determined using gas equilibration studies and X-ray diffraction methods, that these materials are not stable below 600°C in percent level CO_2 environments. The $\text{SrZr}_{0.9}(\text{Y, RE})_{0.1}\text{O}_3$ materials were found to be stable to percent level CO_2 levels. These findings indicate that the cerate compounds suitability for separation applications is limited to noncarbonaceous materials, for example, tritiated water electrolysis.

Conclusions

The measured tritium ion conductivities of $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ and $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ are consistent with a semi-classical model for the proton migration. The reasonably high values of tritium conductivity (bulk + grain boundary) measured for the $\text{BaCe}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ ($\sigma_{\text{T}} = 1 \text{ mS/cm}$ at 600°C) and $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{2.95}$ ($\sigma_{\text{T}} = 0.7 \text{ mS/cm}$ at 600°C) samples could lead to their application as tritium separation membranes. These electrochemical reactors could have potential application in tritium recycling, environmental clean up and waste mitigation of tritiated water and hydrocarbons.

Publications

1. Mukundan, R.; Brosha, E.L.; Birdsell, S.A.; Costello, A.L.; Garzon, F.H.; Willms, R.S. "Tritium conductivity and isotope effect in proton-conducting perovskites". *Journal of the Electrochemical Society*; ; vol.146, no.6, p.2184-7 (1999)

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- [2] A. S. Nowick, A. V. Vaysleyb, *Solid State Ionics*, **97**, 17 (1997)
- [3] W-K Lee, A. S. Nowick and L. A. Boatner, *Solid State Ionics*, **18/19**, 989 (1986)
- [4] Minhui Zheng and Bo Zhu, *Solid State Ionics*, **80**, 59 (1995)

Chemical Composition	X; when quenched from 600°C in 2%H ₂ /3%H ₂ O/Argon; and (% occupancy of oxygen vacancies)	X (when quenched from 600°C in 2%D ₂ /3%D ₂ O/Argon) and (% occupancy of oxygen vacancies)
SrCe _{0.95} Yb _{0.05} (H/D) _x O _{2.975+x/2}	H = 0.01±0.005 (20%)	D = 0.01±0.005 (20%)
SrZr _{0.9} Yb _{0.1} (H/D) _x O _{2.95+x/2}	H = 0.02±0.005 (20%)	D = 0.02±0.005 (20%)
BaCe _{0.9} Yb _{0.1} (H/D) _x O _{2.95+x/2}	H = 0.04±0.005 (40%)	D = 0.04±0.005 (40%)

Table 1. Proton and deuteron concentrations measured by thermal gravimetric analysis

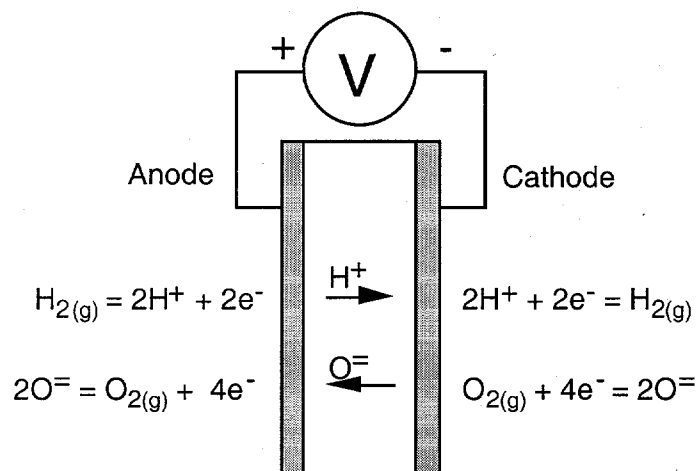


Fig. 1 Schematic illustration of the redox processes of the conduction of protons (and oxygen ions if the oxide exhibits mixed conduction) through a solid electrolyte.

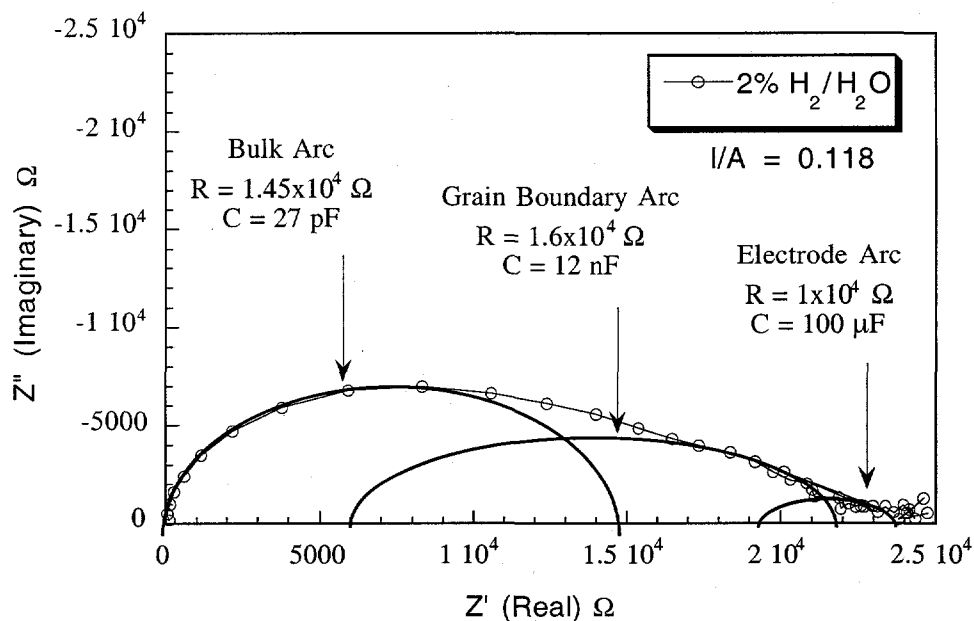
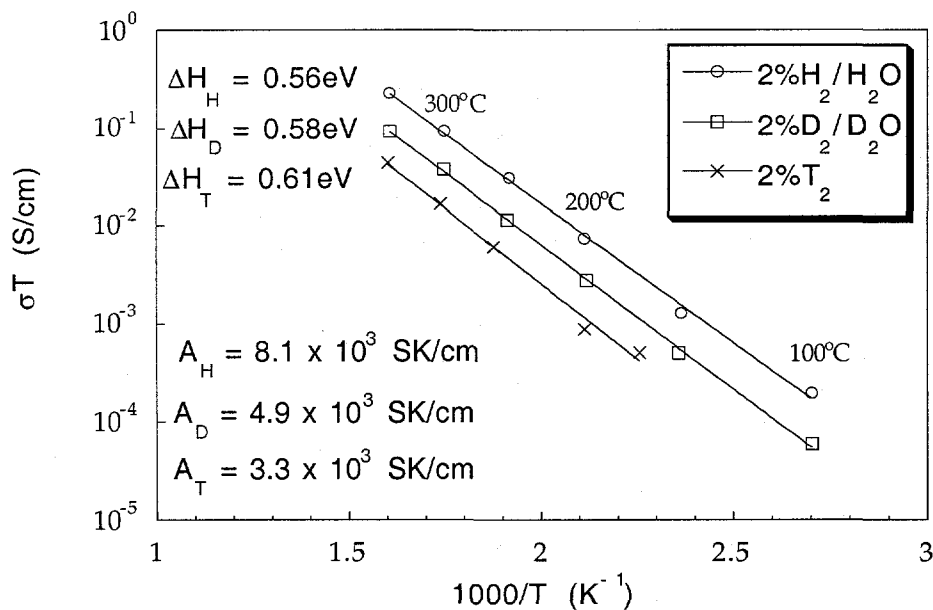


Fig. 2. AC impedance plot of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{2.975}$ at 250°C , the circles drawn in the figure, are for clarity only and are not actual representation of the circuit elements.

a)



b)

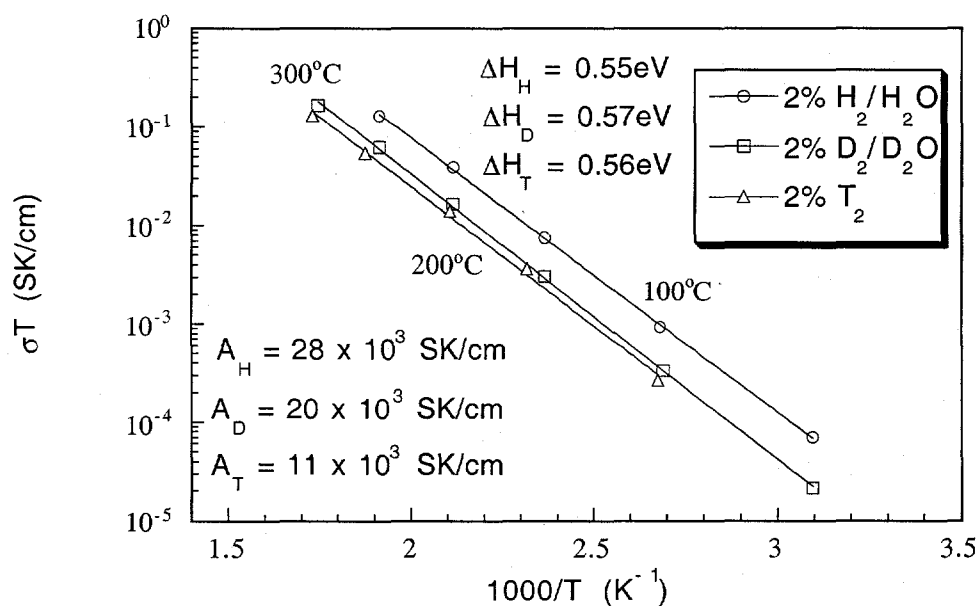


Fig. 3. Arrhenius plot of the conductivity of a) $SrZr_{0.9}Yb_{0.1}O_{2.95}$ and b) $BaCe_{0.9}Yb_{0.1}O_{2.95}$ in H_2 , D_2 and T_2 containing atmospheres

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