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Mixed Conduction in $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ Ceramic

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$\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ ceramic was synthesized by high temperature solid-state reaction. The structural characteristics and the phase purity of the crystal were determined using powder X-ray diffraction analysis. By using the methods of AC impedance spectroscopy, gas concentration cell and electrochemical pumping of hydrogen, the conductivity and ionic transport number of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ were measured, and the electrical conduction behavior of the material was investigated in different gases in the temperature range of 500-900 °C. The results indicate that the material was of a single perovskite-type orthorhombic phase. From 500 °C to 900 °C, electronic-hole conduction was dominant in dry and wet oxygen, air or nitrogen, and the total conductivity of the material increased slightly with increasing oxygen partial pressure in the oxygen partial pressure range studied. Ionic conduction was dominant in wet hydrogen, and the total conductivity was about one or two orders of magnitude higher than that in hydrogen-free atmosphere (oxygen, air or nitrogen).

Key words: $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$, AC impedance, Gas concentration cell, Electrochemical pumping of hydrogen, Mixed conduction

I. INTRODUCTION

It has been about two decades since the first discovery of protonic conduction in ABO_3 perovskites by Iwahara *et al.* [1]. Since then, considerable research on proton conduction in such ceramics has been carried out. These materials are especially interesting because of their potential applications as electrolytes in solid oxide fuel cells, hydrogen sensors, membrane separators and membrane reactors, etc. [2-4]. In contrast to low temperature protonic conductors (e.g. $\text{H}_3\text{Mo}_{12}\text{PO}_{40}\cdot 29\text{H}_2\text{O}$ [5], CsHSO_4 [6]), these oxides do not have hydrogen as a major constituent, but a subsequent exposure of these materials to humid atmospheres is presumed to lead to the incorporation of hydroxyl groups onto oxygen vacant sites, and additional protons are incorporated at interstitial sites to maintain the overall charge balance. Thus, it is considered that a premise to obtain high temperature protonic conductors is to have O-vacancies in the ceramics [7-9].

Among the ABO_3 perovskites studied, BaCeO_3 materials exhibit good protonic conduction over the wide temperature range of 300-1000 °C by substituting trivalent cations such as Y^{3+} , Nd^{3+} , and Gd^{3+} on some Ce^{4+} sites [10-12]. As a result, they are receiving considerable attention. For Pr-doped perovskite oxides it has been shown that cathode performance is high at intermediate temperature [13], which plays an important role for the study of the conduction properties of the materials. Shuk and Greenblatt synthesized and investigated $\text{Ce}_{1-y}\text{Pr}_y\text{O}_{2-\delta}$, and demonstrated that when Pr

contents was greater than 25%, the electronic conductivity of the system $\text{Ce}_{1-y}\text{Pr}_y\text{O}_{2-\delta}$ exceeded that of the ionic conductivity at temperatures ≤ 700 °C [14]. Fagg and Marozau [15] synthesized and investigated $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ ceramic, discovering that the material was predominantly ionic conductor at elevated temperatures, and the ionic transport number decreased with decreasing temperature in the oxygen partial pressure gradient 101/21.2 kPa (oxygen/air). However, there has been no detailed work done to study the synthesis and the electrical properties of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ solid electrolyte up to the present time.

Usually, for $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$, the solubility limit of M to Ce site, x , is less than 0.2, and the conductivity of $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$ increases with increasing x [16]. In this work, $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ solid electrolyte was selected and synthesized by high temperature solid-state reaction. The structural characteristic and the phase purity of the crystal were determined using powder X-ray diffraction analysis. The electrical conduction behavior of the material was investigated electrochemically in wet hydrogen, wet and dry oxygen, air and nitrogen in the temperature range of 500-900 °C.

II. EXPERIMENTS

$\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ ceramic was synthesized by solid-state reaction method [17]. The desired amounts of Ba $(\text{CH}_3\text{COO})_2$ (purity 99.0%), CeO_2 (99.95%), and $\text{Pr}_2(\text{CO}_3)_3$ (99.95%) reagents were fully mixed in ethanol with an agate mortar and dried. The mixed powders were calcined at 1250 °C for 10 h in air. The obtained oxides were ground in ethanol using a planetary ball mill machine with an agate mill container and agate balls at 150 revolutions per minute for 5 h and dried by an infrared lamp, followed by sieving

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(0.15 mm). The powders were pressed into pellets (diameter of 15 mm, thickness of 2 mm) by a hydrostatic pressure of 10 MPa, and sintered at 1550 °C for 20 h in air. The dense ceramic was thus obtained.

The structural characteristic and the phase purity of the crystal were determined at room temperature by powder X-ray diffraction analysis using a nickel filtered Cu K α_1 radiation (Rigaku D/MAX-III C X-ray diffractometer). The sinters were processed into thin discs with a diameter of 14 mm and a thickness of 0.6 mm, and porous platinum electrodes were attached onto two faces of the discs by firing at a certain temperature. Using these disks, the following gas concentration cells were constructed:

gas (I), Pt|BaCe_{0.8}Pr_{0.2}O_{3-α}|Pt, gas (II)
in which gas represents oxygen, air, nitrogen, hydrogen or water vapor. The electromotive forces (EMFs) of the cells were measured in the temperature range of 500-900 °C.

To identify the protonic conduction in the material directly, electrochemical hydrogen permeation (hydrogen pumping) through the material was performed. In this experiment, hydrogen evolution rate at the cathode of the following cell

(+) wet H₂, Pt|BaCe_{0.8}Pr_{0.2}O_{3-α}|Pt, dry Ar (-)
was measured as a function of direct current passing from anode to cathode. The generated hydrogen at the cathode was carried into a gas chromatography detector, where the concentration of hydrogen was determined and the evolution rate of hydrogen was evaluated.

By AC impedance spectroscopy method over the frequency range of 12-10⁵ Hz using a ZL5-Intelligent LCR measurer (made in Shanghai), the resistances of the material were measured in the temperature of 500-900 °C in dry and wet gases (oxygen, air, nitrogen, and hydrogen) respectively. The conductivity σ of the material under these conditions was calculated from the formula:

$$\sigma = \frac{L}{R \cdot S}$$

where L is thickness of the disc electrolyte, R is resistance, and S is the electrode area.

III. RESULTS AND DISCUSSION

A. Characterization

Figure 1 shows the powder XRD pattern of BaCe_{0.8}Pr_{0.2}O_{3-α} ceramic. By comparison with the standard XRD data of BaCeO₃ in JCPDS, the positions and intensities of the diffraction peaks were found basically in agreement with those in JCPDS. Thus the material can be classified as a perovskite-type BaCeO₃ orthorhombic system. The relative density determined by mass, unit cell volume and lattice parameter of the ceramic is higher than 90%. The experiment proved that the material could not be permeated by oxygen, air, nitrogen or hydrogen.

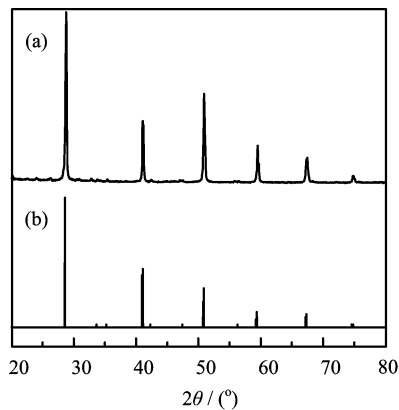


FIG. 1 (a) Powder XRD pattern of BaCe_{0.8}Pr_{0.2}O_{3-α} sinter and (b) XRD pattern of BaCeO₃ in JCPDS.

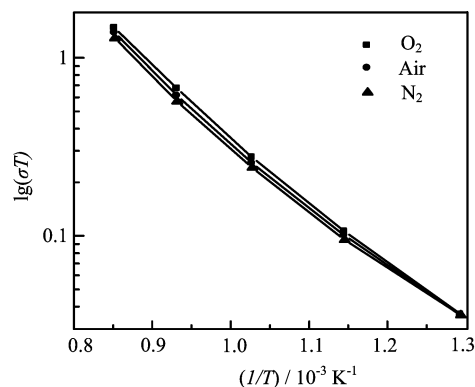
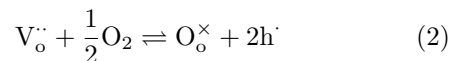
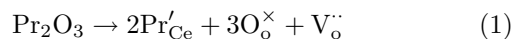


FIG. 2 Conductivities of BaCe_{0.8}Pr_{0.2}O_{3-α} in dry gases.

B. Electrical conductivities in dry gases

Figure 2 displays the Arrhenius plots of the total conductivities of BaCe_{0.8}Pr_{0.2}O_{3-α} in dry oxygen, air and nitrogen from 500-900 °C. It is clear from Fig. 2 that $\lg(\sigma T)$ increases basically linearly with the reciprocal of the temperature, indicating there is no phase change under the experimental conditions. At 500 °C, the total conductivities of the material are close to each other in dry oxygen, air, and nitrogen, but they increase slightly with increasing oxygen partial pressure from 600-900 °C. At 900 °C, the total conductivity of BaCe_{0.8}Pr_{0.2}O_{3-α} is about 1.0-1.3 mS/cm in the oxygen partial pressure range of 7.9×10^{-5} – 1.1×10^5 Pa. The electrical conduction behavior of the material in dry oxygen and air can be explained by the two following defect reactions [17,18].



From reaction (1), it is apparent that when some Ce⁴⁺ are replaced by Pr³⁺, to keep the electric charge balance, a certain amount of oxide ionic vacancy is produced. At dry higher oxygen partial pressure, the disso-

lution of oxygen into the lattice produces lattice oxide ion and electronic holes at the expense of oxide ionic vacancies due to reaction (2). In this case, the charge carriers are oxide ions and electronic holes. Thus, the material shows mixed conduction of oxide ions and electronic holes in dry oxygen and air. To clarify the oxide ionic contribution under dry oxygen-containing atmosphere, the EMF of the oxygen concentration cell in dry atmosphere using the material as solid electrolyte was measured in the range 500-900 °C. The results are shown in Fig.3, in which the broken line stands for the theoretical values at each temperature, and the solid line with marks stands for the observed ones. It is seen from Fig.3 that the observed EMF values of the concentration cell based on $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ are much lower than the theoretical ones. The oxide ionic transport numbers given by the ratio of the observed EMF versus the theoretical EMF are 0.10-0.25, indicating that oxide ionic conduction is very low while electronic hole conduction is dominant in the material in dry oxygen-containing atmosphere. With increasing temperature, the concentration of oxide ions increases. In addition, the material may obtain oxygen because of the different chemical valences (+3, +4) of Ce and Pr, so many more oxide ionic vacancies are produced [18]. Thus the total conductivities of the material increase with increasing temperature.

The change of the conductivity with temperature in dry nitrogen ($p_{\text{O}_2}=79 \mu\text{Pa}$) is similar to that in dry oxygen or air, indicating the same conduction mechanism in dry oxygen, air or nitrogen. The material may show mixed conduction of oxide ions and electronic holes in dry nitrogen from 500-900 °C and electronic hole conduction is dominant.

According to the reaction (2), the concentration of oxide ions and electronic holes increases with increasing oxygen partial pressure. At the same time, the concentration of oxide ionic vacancies decreases. In addition, the material may obtain oxygen in dry oxygen-containing atmosphere at elevated temperature because of the different chemical valences (+3, +4) of Ce and Pr, thus resulting in a slow increase of the total conductivity of the material with oxygen partial pressure in the pressure range studied [18].

C. Electrical conductivities in wet gases

Figure 4 shows the Arrhenius plots of the total conductivities of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ in wet gases from 500-900 °C. It is seen from Fig.4 that the total conductivity of the material in wet hydrogen-free atmosphere (oxygen, air or nitrogen) increases slightly with increasing oxygen partial pressure from 500-900 °C, which is similar to that in dry gases. At 900 °C, the total conductivity of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ is about 0.71-1.3 mS/cm in the oxygen partial pressure range studied, which is somewhat lower than that in dry gases. This tendency is consistent with the experimental results of

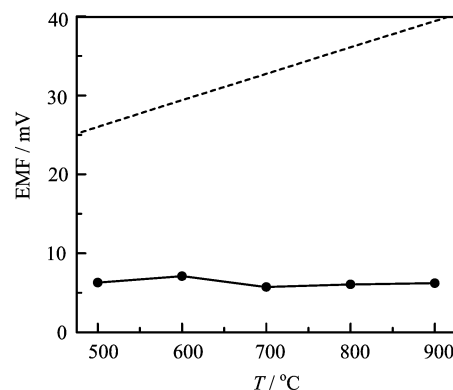


FIG. 3 EMF of the oxygen concentration cell: air(dry), $\text{Pt}|\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}|\text{Pt},\text{O}_2(\text{dry})$ at different temperatures.

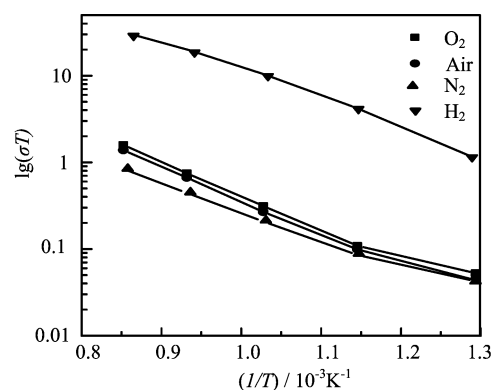


FIG. 4 Conductivities of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ in wet gases ($p_{\text{H}_2\text{O}}=3.2 \text{ kPa}$).

$\text{Ba}_x\text{Ce}_{0.90}\text{Y}_{0.10}\text{O}_{3-\alpha}$ material obtained by Ma *et al.* [19]. The total conductivity of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ in wet hydrogen-free atmosphere is about one or two orders of magnitude lower than that in wet hydrogen atmosphere (27 mS/cm, 900 °C). However, the conductivity of Y-doped BaCeO_3 (BCY) in air or oxygen is even higher than that in hydrogen as reported in the literature [19]. This indicates that doping Pr and Y have different effects on electrical conduction of BaCeO_3 -based material. For Pr-doped BaCeO_3 , the material may lose oxygen because of the different chemical valences (+3, +4) of Pr at high temperature, so many more oxide ionic vacancies and electronic holes are produced, causing the increase of the total conductivities of the material [18]. The phenomenon is more obvious in wet hydrogen atmosphere. Thereby the conductivities of $\text{BaCe}_{0.8}\text{Pr}_{0.2}\text{O}_{3-\alpha}$ in air or oxygen are lower than that in wet hydrogen [18]. For BCY, the conductivity of BCY in air or oxygen is higher than that in wet hydrogen because of the constant chemical valences (+3) of Y [19].

In order to clarify the oxide ionic contribution to conductivity under wet oxygen-containing atmosphere, the EMF of the oxygen concentration cell using the material as solid electrolyte in these atmospheres was measured

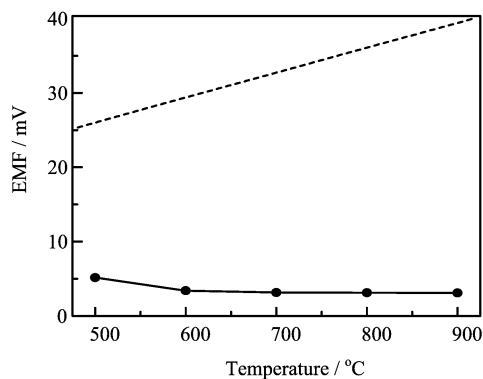


FIG. 5 EMF of the oxygen concentration cell: air(wet), Pt|BaCe_{0.8}Pr_{0.2}O_{3-α}|Pt,O₂(wet) at different temperatures.

at 500-900 °C, the results were shown in Fig.5. It can be seen from Fig.5 that the observed EMF values of the concentration cell based on BaCe_{0.8}Pr_{0.2}O_{3-α} are much lower than the theoretical ones, indicating that the oxide ionic conduction in the material is also very low under wet oxygen-containing atmosphere. The oxide ionic transport numbers are 0.06-0.20, slight lower than those in dry oxygen-containing atmosphere, which may result in the total conductivity in wet hydrogen-free atmosphere (oxygen, air or nitrogen) being slight lower than that in dry gases.

To investigate protonic contribution to the total conductivity of the material in wet oxygen-containing atmosphere, the following steam concentration cell using the material as solid electrolyte was constructed: air(*p'*_{H₂O}),Pt|BaCe_{0.8}Pr_{0.2}O_{3-α}|Pt,air(*p''*_{H₂O}), where, *p'*_{H₂O}>*p''*_{H₂O}. Water vapor pressure *p'*_{H₂O} and *p''*_{H₂O} were controlled by letting air pass through water at 10.4 and 0.0 °C, respectively.

The EMF values of the water steam concentration cell are much smaller than the theoretical ones, the protonic transport number is 0.00-0.15, suggesting the material shows very low protonic conduction under wet oxygen-containing atmosphere. The above results suggest that electronic hole conduction should be dominant in BaCe_{0.8}Pr_{0.2}O_{3-α} under wet oxygen-containing atmosphere. The change of the conductivity with temperature in wet nitrogen is similar to that in wet oxygen or air, indicating that the same kind of charge carrier in these cases. The material may show mixed conduction of protons, oxide ions and electronic holes in wet nitrogen at 500-900 °C and electronic hole conduction is dominant. In wet hydrogen, hydrogen incorporation into perovskite-type oxides as illustrated by reaction (3) to reaction (5).

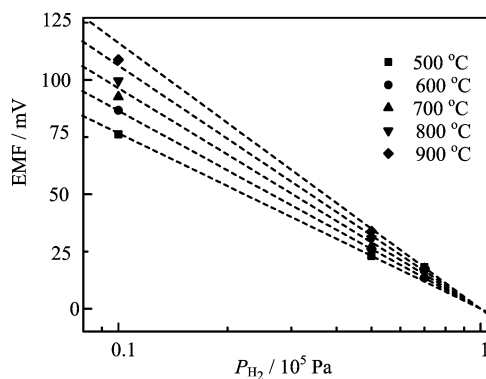
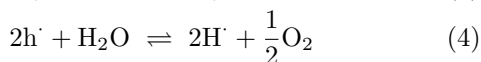
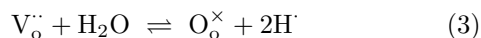
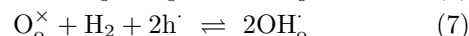
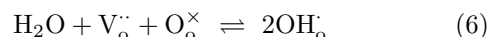


FIG. 6 EMF of the hydrogen concentration cell: H₂(wet), Pt|BaCe_{0.8}Pr_{0.2}O_{3-α}|Pt,H₂-Ar(wet).

Reaction (3) and reaction (5) may be written as:



where OH_o[·] is hydroxide which represents an interstitial proton associating with a neighbor oxide ion. When BaCe_{0.8}Pr_{0.2}O_{3-α} is exposed to wet hydrogen, the reaction (2) will shift to the left because of the very low level of oxygen partial pressure. At the same time, the concentration of oxygen vacancies increases, and reactions (6) and (7) shift to the right, thus resulting in a significant increase of conductivities in wet hydrogen [20,21]. In addition, the increase of the conductivities in wet hydrogen is caused by the different chemical valences (+3, +4) of Ce and Pr as described above.

To clarify the ionic conduction in wet hydrogen, the EMF of the hydrogen concentration cell using the material as solid electrolyte was measured at 500-900 °C. In each experiment, hydrogen (10⁵ Pa) and a mixture of hydrogen and argon were supplied to the anode and cathode compartments, respectively. The water vapor pressure in both gases was kept constant (*p*_{H₂O}=2.3 kPa). The results are shown in Fig.6, in which the broken line stands for the theoretical values at each temperature, based on Nernst's equation and the assumption that the material is pure ionic conductor. It is evident from Fig.6 that the observed EMF values are in accordance with the theoretical ones in the range 500-600 °C and the ionic transport number is 1, suggesting that BaCe_{0.8}Pr_{0.2}O_{3-α} should be a ionic conductor under such conditions and temperatures. Above 600 °C, the observed EMF values are lower than the theoretical ones and the ionic transport number is 0.93-0.96, indicating that the material is a mixed conductor of ions and electrons, but ionic conduction is dominant.

In order to confirm the protonic conduction in the material directly, electrochemical hydrogen permeation (hydrogen pumping) using the material as a solid electrolyte was carried out. If the material is protonic conductor, then when a direct current is sent to the cell, H₂ will become protons by losing electrons on the an-

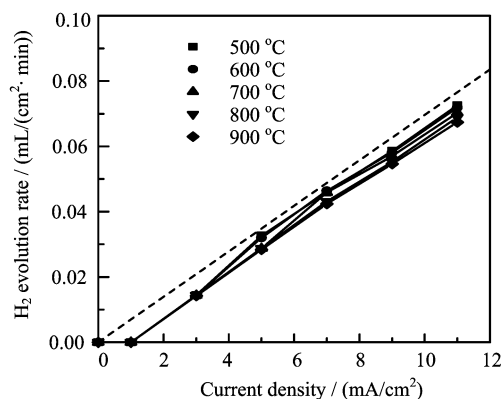


FIG. 7 Electrochemical evolution rate of H_2 .

ode surface, which permeate through the material to the cathode where protons obtain electrons and turn into H_2 . The generated hydrogen at the cathode can be detected by gas chromatography and the hydrogen evolution rate can be calculated. The theoretical rate was obtained based on Faraday's law and the assumption that the charge carriers in the ceramic are only protons [22,23].

Figure 7 is the electrochemical evolution rate of hydrogen pump: (+) wet H_2 , Pt|BaCe_{0.8}Pr_{0.2}O_{3- α} |Pt, dry Ar (-). The cathode gas (Ar) was dried by passing through P₂O₅, and the anode gas (H_2) was saturated with water vapor at normal temperature, at a flow rate of 30 mL/min. As shown in Fig.7, the hydrogen evolution rates increase with increasing current densities imposed on the hydrogen pump under all temperatures, which directly supports the idea that the material has an ability to transfer protons. When the current densities are lower than 1 mA/cm², the hydrogen evolution rates are almost zero, perhaps because the little hydrogen evolved at the cathode under these conditions is exhausted in reacting with the little oxygen left in Ar and producing water [24-26]. The possibility of the partial oxide-ionic conduction cannot be omitted due to the existence of little oxygen left in Ar. But, it may be considered that the contribution of the oxide ions to the total ionic current is small because the amount of the oxygen left in Ar is small. The proton transport numbers can be evaluated from the ratio of the observed rate against the theoretical rate under certain temperature: they are about 1 at 500-600 °C, about 0.93 at 700-900 °C, which are basically in agreement with those obtained by the hydrogen concentration cell method.

IV. CONCLUSION

BaCe_{0.8}Pr_{0.2}O_{3- α} solid electrolyte is a single phase of perovskite-type orthorhombic structure. In the range of 500-900 °C, electronic-hole conduction is dominant in dry and wet oxygen, air or nitrogen, and the total conductivity of the material increased slightly with in-

creasing oxygen partial pressure in the oxygen partial pressure range studied. Ionic conduction is dominant in wet hydrogen, and the total conductivity is about one or two orders of magnitude higher than that in hydrogen-free atmosphere (nitrogen, air or oxygen).

V. ACKNOWLEDGMENTS

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