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Dissolution and Release Behavior of Hydrogen Isotopes from Barium-Zirconates

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ABSTRACT: *Hydrogen release behavior from perovskite proton conducting oxide, yttrium doped barium-zirconate, $BaZr_{0.9}Y_{0.1}O_{3-\alpha}$ (BZY) exposed to D_2 or D_2O atmosphere was studied by thermal desorption spectroscopy (TDS) detecting deuterium gas (D_2) and heavy water vapor (D_2O) separately. The release of hydrogen appeared at around 950-1175 K. Hydrogen solubility was higher in the BZY sample exposed to the D_2O.*

Keywords: Barium-zirconate, perovskite oxide, hydrogen dissolution, hydrogen solubility, TDS.

1. INTRODUCTION

Perovskite oxides-based proton and electronics conducting ceramic membrane has drawn considerable attention for hydrogen separation applications over the last few decades due to several advantages like thermal stability, good mechanical strength, high hydrogen permeation flux, and chemical resistivity in corrosive environments [1,2]. The extensively studied Pd-based membranes showed poor stability and high cost of Pd, whereas conventional membranes of proton conducting materials exhibit much lower hydrogen permeation. Comparing all proton-conducting oxides, as the temperature increased $BaCeO_3$ based perovskite shows the highest conductivity with the contribution of ionic conduction of oxygen [3]. The improvement of perovskite oxides membrane proton conducting properties is essential to consider trivalent rare-earth atom at B-site. Tan et al. (2012) [4] focused on Tb-doped $BaCeO_3$ ($BaCe_{0.95}Tb_{0.05}O_{3-\alpha}$) based perovskite oxides having higher proton conductivity but lower electronic conductivity. The effective way of promoting hydrogen permeation flux is to reduce membrane thickness and the sintering process of the membrane. Throughout the last few decades: the ceramic membranes of hollow fiber geometry have been used to design and develop with the inclusion of combined phase inversion and sintering technique, because of high-temperature scaling, thin effective membrane thickness and larger membrane area as per unit packing volume. The rate of high hydrogen production is possible to achieve using a hollow fiber membrane module at large specific membrane areas irrespective of the lower permeability of the individual membrane.

Low-level tritium detection is an imperative issue in tritium handling facilities due to their potential radioactive properties. In recent times, the development and utilization of various tritium monitors to control the radiation have been reported [5]. In addition, to improve the performance of the tritium monitor in terms of low concentration tritium detection, the implication of hydrogen pump as a membrane separator which consists of proton conducting oxide has been proposed by Tanaka et al. (2008) (**Fig. 1**) [6]. The research group used $CaZr_{0.9}In_{0.1}O_3$−α as proton conducting oxide to recover the low concentration tritium [7]. In the next comprehensive study, the tritium monitor's technical feasibility was investigated by the integration test of the system consisting of a proportional counter combined with an electrochemical hydrogen pump [8].

As proton-conducting oxides are promising materials for electrochemical devices like fuel cell, hydrogen pump, hydrogen sensor, and for nuclear fusion reactor's tritium purification [9–14], recovery [10,15–19], and monitoring system, therefore, the study of hydrogen behavior in such oxide materials is very fundamental and important. Yttrium (Y) doped barium-zirconate ($BaZrO_3$) is a proton-conducting oxide that has a perovskite structure [20]. In this study, the dissolution of hydrogen in BZYC specimens was done using D_2 gas and D_2O vapor

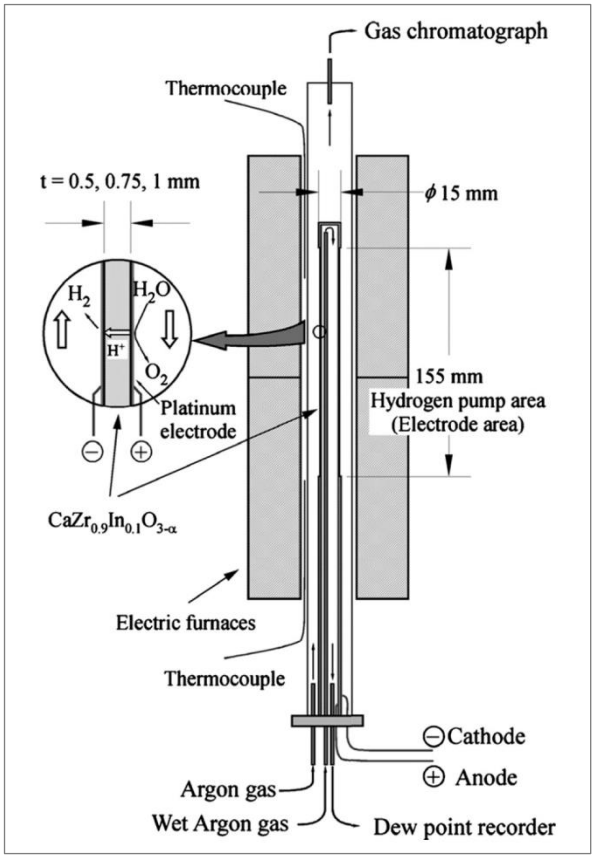

Fig. 1. Schematic of the hydrogen pump apparatus consists with proton-conducting oxide for the tritium monitoring. Reproduce with permission from Ref. [6].

separately. Then the hydrogen release and hydrogen solubility were investigated by the thermal desorption spectroscopy (TDS) method.

2. EXPERIMENTAL

2.1 Sample preparation

The disc shape specimen (diameter: 7.7 mm, thickness: 2.2 mm) was prepared using a conventional powder sintering method at 1923 K for 20h, which is described elsewhere [16,21–23]. The SEM and EDX mapping were performed before and after polishing the sample to understand its surface properties. All chemical components of the specimen were uniformly distributed throughout the surface after polishing. The sintered disc specimen was cut using a diamond saw into parallelepiped pieces (7.7 x 2.2 x 0.5 mm^3) for D_2 gas or D_2O vapor exposure and TDS study.

2.2 D_2 and D_2O exposure

The cut sample was placed in a quartz glass tube and evacuated to low pressure (~10^{-6} Pa). At a temperature of

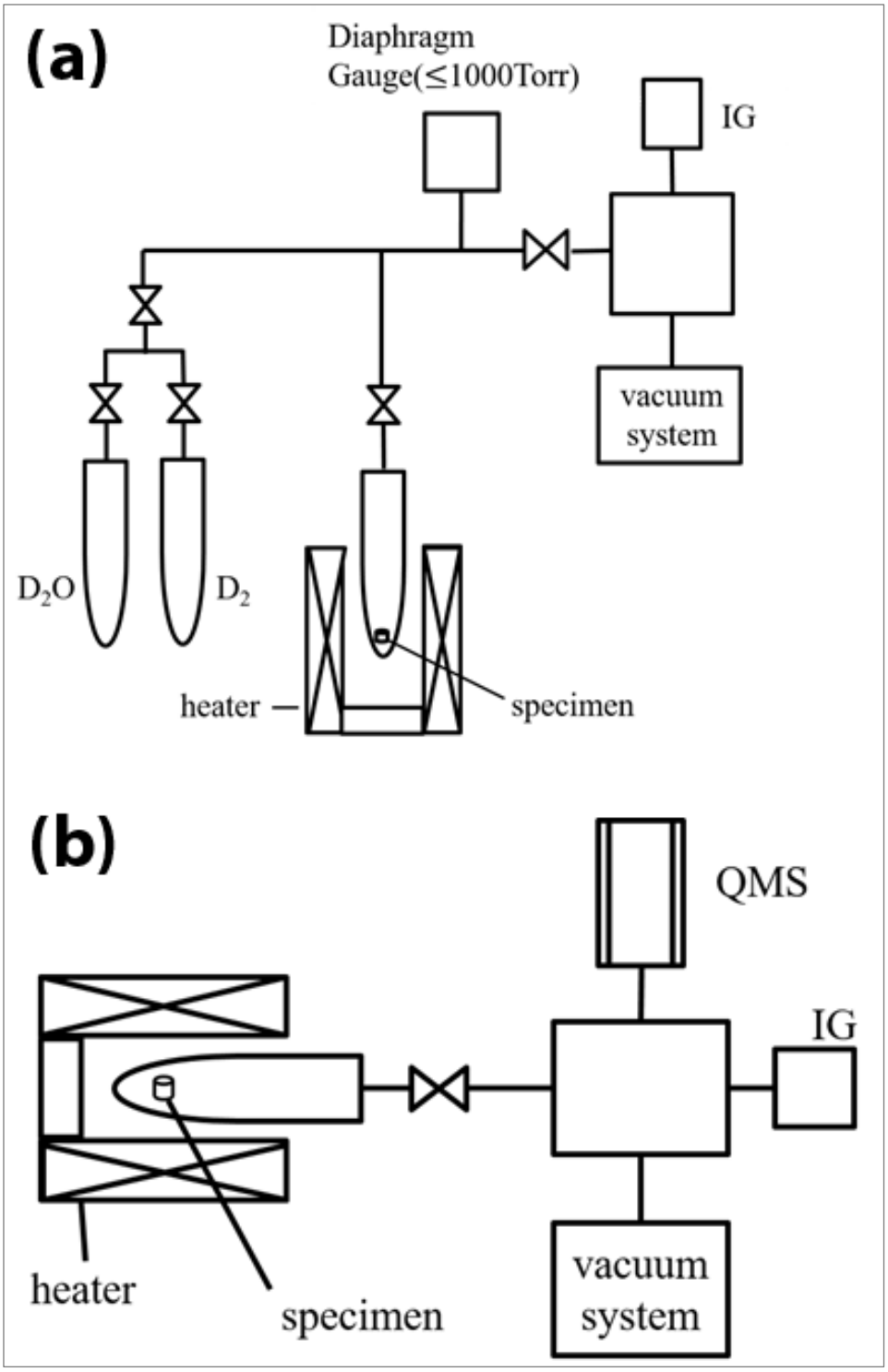

Fig. 2. (a) Schematic of D_2 gas and D_2O vapor exposure apparatus, (b) schematic of temperature programmed desorption (TDS) system.

1273 K, vacuum annealing was performed for 30 min to remove the sample's volatile substances. Then at 873 K, deuterium gas (D_2, 1.3 kPa) was exposed to the sample for 1 h using the apparatus shown in Fig. 2(a) [21]. After the exposure, the quartz glass tube was quenched with room temperature water. Finally, the sample was taken out from the quartz glass tube after recovering the D_2 gas. The same sample was used repeatedly for heavy water vapor (D_2O, 1.3 kPa) exposure and the TDS study.

2.3 D_2 and D_2O measurement

The TDS apparatus used in this experiment to measure the released hydrogen (D_2, HD, D_2O and HDO) from the D_2 gas and D_2O vapor exposed sample is shown in Fig. 2(b) [2]. First, the quartz glass tube baking without the sample was performed with an electric furnace to release and remove substances accumulated in the device at 1273 K for 30 min. After cooling down the glass tube to room temperature, the D_2 gas exposed sample was placed in the TDS study's glass tube. Then after evacuating the glass tube to low pressure (~10^{-6} Pa), the temperature of the sample was allowed to raise (at a heating rate of 0.5 K/s) up to 1273 K. After 30 min stays at 1273 K, the heater power was disconnected automatically by using a programable temperature controller. The gas released from the samples was measured using a quadrupole mass spectrometer (Q-MAS) (TSPTT200, INFICON) [24] during this sample heating and cooling down cycle. The above same procedure was also applied for the D_2O exposed sample.

2.4 QMAS data conversion using He-standard leak

The mass spectrometer is one of the most popular instrumental analyzers that ionizes and separates chemical substances such as atoms and molecules, and finally measures the generated ions by their mass. The major parts of a mass spectrometer are the ionization part (ion source), mass analysis part (analyzer), detection part (detector), vacuum exhaust part (vacuum pump), device control part, data processing part (data system), etc. There are various types of analyzers, one of which is a quadrupole, and a mass spectrometer having a

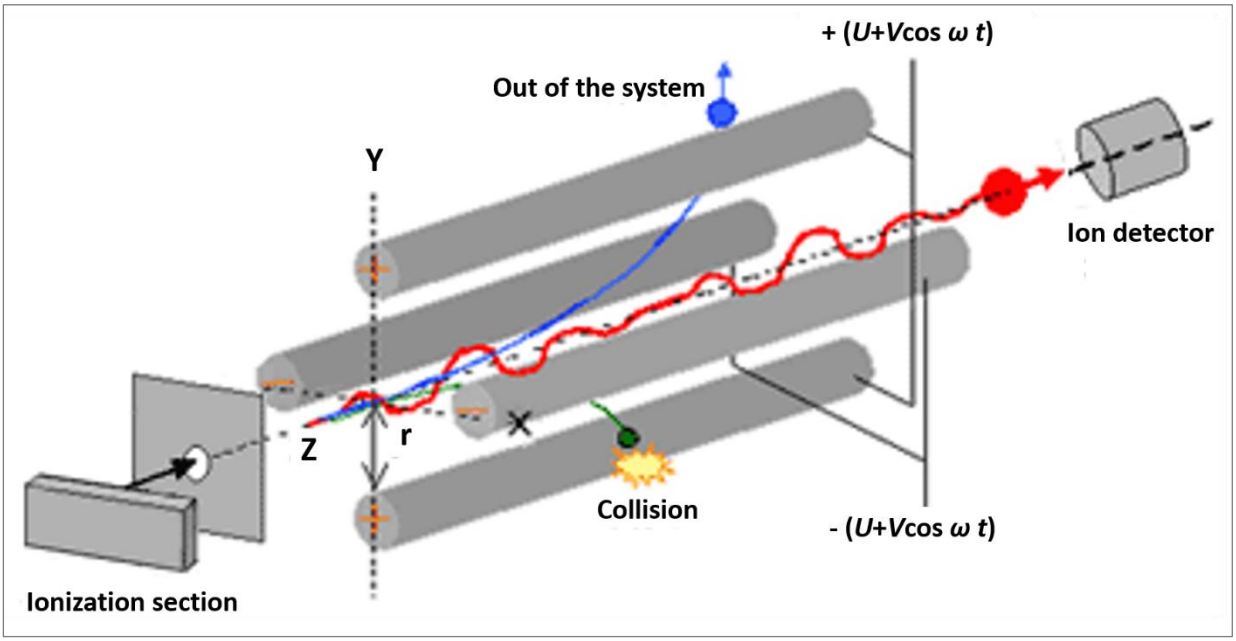

Fig. 3. Conceptual diagram of ion separation and detection in a quadrupole analyzer.

Fig. 4. Figure 13 He standard leak (Vacuum Technology Inc., Model: CL-6-He-4FVCR-500DOT-MFV).

quadrupole analyzer is known as quadrupole mass spectrometer (QMAS). The features of QMS are: 1. low vacuum (usually ~10^{-5} Torr), 2. miniaturization, 3. high-speed scanning (latest is 10000*u*/sec or more, *u* = unified atomic mass unit), 4. cheap, 5. easy to operate, 6. robust, and easy to maintain, and many other advantages.

A QMAS consists of four parallel rod-shaped electrodes (**Fig. 3**) where a superposition of DC voltage and high-frequency AC voltage, $\pm(U+V\cos\omega t)$ is applied in the opposite electrodes having the same polarity and forms a quadrupole electric field (where U is the DC voltage, V is the maximum value of the AC voltage, $\omega = 2\pi\nu$, ν is the high frequency). In mass spectrometry, gas molecules are ionized under a high vacuum, and the generated ions are separated and analyzed in the order of charge. When ions enter the quadrupole electrode, they are affected by the high-frequency electric field and travel in the z direction while oscillating in the x or y direction (**Fig. 3**). But only ions with a specific *m*/*z* value make stable oscillatory motion, pass through the quadrupole, and reach the detector. On the other hand, ions with other *m*/*z* values have large amplitude and diverge and collide with the electrode. When the frequency f is constant and U/V have a certain value, only ions satisfying $m/z = 0.14\ V/f^2r^2$. Therefore, if V is continuously changed while U/V is kept constant, ions corresponding to each mass will be separated and

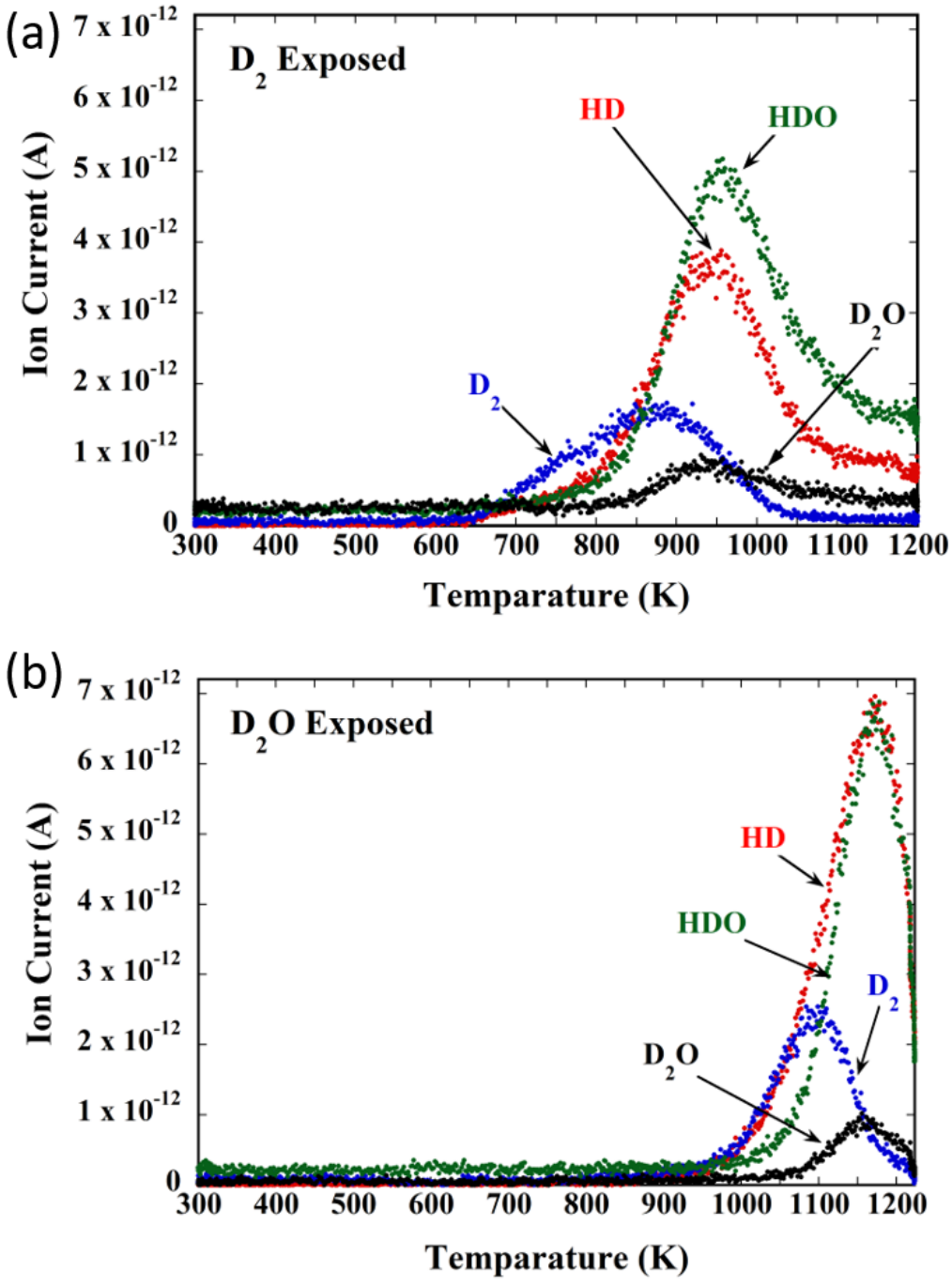

Fig. 5. TDS results for (a) D_2 gas, and (b) D_2O vapor exposure samples.

the magnitude of the ratio *m*/*z*, where *m* = mass, and *z* =

Table 1. D amount released from D_2 and D_2O exposed samples.

Deuterium (D) amount	D_2 exposed sample	D_2O exposed sample
D from D_2 and HD (D/M)	5.5×10^{-5}	1.4×10^{-3}
D from D_2O and HDO (D/M)	7.5×10^{-5}	1.1×10^{-3}
Total D (D/M)	1.3×10^{-4}	2.5×10^{-3}
Fraction of deuterium gas (%)	42	56
Fraction of water vapor (%)	58	44

detected. The passing ion stream is usually detected by an electron amplifier tube. In the electron amplifier tube, a small number of incident ions hit the metal surface and emit a large number of secondary electrons. By repeating this, secondary electrons are multiplied, and a small number of ions can be detected with high sensitivity.

A standard He leak experiment was carried out to convert the measured current value obtained from Q-MAS data into the amount of emission. The leaked amount of He standard leak (Company name: Vacuum Technology Inc., Model: CL-6-He-4FVCR-500DOT-MFV, Serial: D15543 (**Fig. 4**)) used in the experiment was 1.8 × 10-7 (Pa・m^3 / s]. Since the inside of the apparatus is evacuated, it is assumed that the state is close to an ideal gas. In that case, from the equation of state of the gas,

$$n = \frac{PV}{RT} = \frac{1.8 \times 10^{-7}}{8.31 \times 297}\left[\frac{\text{Pa m}^3\ \text{s}^{-1}}{\text{J K}^{-1}\ \text{mol}^{-1}\ \text{K}}\right] = 7.46 \times 10^{-11}[\text{mol/s}] \quad (8)$$

The leak rate (n) of the He standard leak is 7.46×10^{-11} [mol⁄s].

3. RESULTS AND DISCUSSION

The ion currents obtained from Q-MAS data for the D_2 gas and D_2O vapor exposed samples are shown in **Fig. 5**. In the case of D_2 exposed sample HD, HDO, and D_2O was released at 950 K whereas D_2 released at 875 K. In the case of D_2O exposed sample HD, and HDO was released at 1175 K whereas D_2 and D_2O were released at 1150 K and 1100 K, respectively. The highest release peak was detected as HDO gas from D_2 exposed sample and there may appear a trend for the hydrogen release as HDO > HD > D_2 > D_2O. On the other hand, the highest peak was observed as HD and HDO vapor from D_2O exposed sample and there may appear a trend for the hydrogen release as HD = HDO > D_2 > D_2O.

The total amounts of D-containing gas released from the D_2 or D_2O exposed samples and its ratios are listed in **Table 1**. The total amount of deuterium (D) released from D_2 exposed sample was 1.3×10^{-4} (D/M), where released deuterium gas and water vapor were ~ 5.5×10^{-5} (D/M) and ~ 7.5×10^{-5} (D/M), respectively. On the other hand, the total amount of D released from D_2O exposed sample was 2.5×10^{-3} (D/M), where released deuterium gas and water vapor were ~ 1.4×10^{-3} (D/M) and ~ 1.1×10^{-3} (D/M), respectively. The percentage of water vapor released from the D_2 exposed sample is higher than that of the D_2O exposed sample, whereas an opposite result appears for deuterium gas release. It is also clear that the total amount of deuterium released from D_2O exposed sample is approximately 20 times more than the D_2 exposed sample. The experiment's obtained result suggests that, under D_2O exposed condition and at 1175 K operating temperature, Y-doped barium-zirconate might be preferable for electrochemical applications due to its higher hydrogen solubility.

4. CONCLUSIONS

In this study, hydrogen (deuterium) was dissolved in $BaZr_{0.9}Y_{0.1}O_{3-\alpha}$ by the exposure of deuterium gas or heavy water vapor, and the amount of dissolved deuterium in the sample was measured by TDS method. It was observed that deuterium solubility is higher in the BZY sample under the D_2O exposure condition and the release of deuterium was appeared at around 1175 K.

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