Journal of Nuclear Materials 386–388 (2009) 342–344

Contents lists available at ScienceDirect

Journal of Nuclear Materials

journal homepage: www.elsevier.com/locate/jnucmat

Dose rate dependence of radiation induced conductivity for hydrogen-doped perovskite ceramics at 473 K

B. Tsuchiya [a,*], A. Moroño [b], S.M. González [b], E.R. Hodgson [b], S. Nagata [a], K. Toh [a], T. Shikama [a]

[a] Institute for Materials Research, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan
[b] Euratom/CIEMAT, Fusion Association, Avenida Complutense 22, 28040 Madrid, Spain

ARTICLE INFO

PACS:
N0100
R0400
H0400
C0300

ABSTRACT

Dose rate dependence of radiation induced conductivity (RIC) of hydrogen doped yttrium-doped perovskite-type barium-cerium oxide ceramics ($BaCe_{0.9}Y_{0.1}O_{3-\delta}$) was investigated under 1.8 MeV electron irradiation within dose rate of 10–1000 Gy/s at temperature of 473 K. The RIC in the initial dose for the H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ exponentially increased as a function of dose rate, and eventually became about three orders of magnitude higher than the base conductivity without radiation. For the dose rates below 200 Gy/s, the RIC of the H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ was higher by one order of magnitude than that of the H-undoped one. The results may show that the RIC takes place due to hydrogen diffusion as well as electronic excitation, enhanced by ionizing effects. For the dose rate range 300–1000 Gy/s, the RIC of H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ is similar to that of H-undoped one. The radiation enhanced diffusion of constitutive oxygen dominates for the RIC.

1. Introduction

So far, it has been reported that the electrical properties of insulating materials such as oxide ceramics are dynamically changed by several radiation induced phenomena [1–6]. It will be predicted that the radiation induced phenomena are further enhanced by behavior of hydrogen isotopes trapped in the insulating materials during long term D–T discharge. Our groups have carried out the electrical conductivity in situ measurements of the insulating materials under reactor irradiation using Japan Materials Testing Reactor at Japan Atomic Energy Agency (JAEA), in order to investigate the hydrogen effects on the radiation phenomena for the typical proton conducting perovskite-type oxide ceramics ($BaCe_{0.9}Y_{0.1}O_{3-\delta}$) [2]. As a result, the increment of the electrical conductivity, called radiation induced conductivity (RIC), was observed as the reactor full nuclear power increased up to 50 MW. The maximum ionizing dose rates were 1.1 and 2.0 kGy/s for hydrogen (H)-doped and -undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$. The irradiation temperatures for the H-doped and -undoped specimens were 426–448 and 473 K during the first cycle at the full power for 29 days and 421–572 and 673 K during the second cycle for 27 days. For 1.1 kGy/s, the RIC of H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ was about two orders of magnitude higher than that of H-undoped one. The result is attributed to hydrogen enhanced diffusion. Moreover, the RIC for H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ in first cycle, initially decreased quickly for a brief period, and hereafter reached a constant level which was kept in second cycle. However, the correlation between the hydrogen behavior and the radiation phenomena is not yet fully understood, since there are some effects such as temperature, neutron elastic cascade collision and electronic excitation by gamma rays in the reactor. It is necessary to separate their effects and make out some experiments with one kind of irradiation, in order to understand the results on the reactor radiation.

In the present study, to clarify the changes in proton and ionic conductions by electronic excitation effects, electrical, proton and ion conductivities of $BaCe_{0.9}Y_{0.1}O_{3-\delta}$, heated at temperature of 473 K, were in situ measured with changing dose rates of 10–1000 Gy/s using 1.8 MeV electron beams from Van de Graaff at Euratom/CIEMAT.

2. Experiments

Y (10 at.%) doped $BaCeO_3$ specimens which had a typical perovskite-type structure and a high proton conductivity at elevated temperatures above 473 K [7] were used in the present experiments. Hydrogen atoms were implanted into one zirconium (Zr) electrode only of 1 μm thick, deposited on both sides of the specimen, using a 10 keV H_2^+ ion beam at room temperature. The fluence was about 1.0×10^{22} H/m^2, and the projected range of 5 keV H^+ in Zr is about 25 nm. It has been confirmed by an elastic recoil detection (ERD) measurements with 2.8 MeV He^{2+} ion probe beams [8] that transport of hydrogen atoms which pass through the interface between zirconium metals and ceramics takes place at

* Corresponding author. Tel.: +81 22 215 2063; fax: +81 22 215 2061.
E-mail address: tsuchiya@imr.tohoku.ac.jp (B. Tsuchiya).

0022-3115/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnucmat.2008.12.133

temperature above approximately 473 K. The H-doped and -undoped specimens were heated up to 473 K in a vacuum chamber, evacuated under a pressure of 1.3×10^{-5} Pa, and irradiated using a 1.8 MeV electron beam from a Van de Graaff accelerator, installed at Euratom/CIEMAT in Spain [5]. The electron irradiation dose rates were within 10–1000 Gy/s. The irradiation temperature at 1000 Gy/s is elevated up to approximately 473 K by electron heating effects. It is a reason why the specimen has been heated at 473 K. Proton conductivity measurements were carried out by recording direct current (DC)-currents while applying DC-voltages of +10 V during irradiation. The DC electric field was disconnected during irradiation, except for the short times needed for the measurements.

3. Experimental results and discussion

Fig. 1(a) and (b) shows radiation induced conductivity, σ_{RIC}, for H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ as a function of ionizing dose rate for 10–200 and 300–1000 Gy/s, respectively, during electron irradiation. The RIC at 10, 50, 100 and 200 Gy/s increases about 1.2, 2.4, 6.3 and 23 times, respectively, higher, as compared base conductivity, $\sigma_{BC,}$ without radiation. The RIC in the initial dose is similar to that in the final one which means that the irradiation time is 60 min, and the dose is different for the several dose rates. On the other hand, the RIC in the initial at 300, 500 and 1000 Gy/s is respectively about 47, 293 and 3485 times as much as those before irradiation, whereas the RIC in the final one changes to be respectively about 36, 130 and 5484 times as much as those after irradiation. The degradation of σ_{RIC} and σ_{BC} is possibly called Radiation Induced Electrical Degradation (RIED) which is generally considered to occur with an electric field during irradiation [4–6]. The RIED phenomenon has been associated with displacement damage and radiation induced impurity diffusion. In the present study the mobilities of dopant Y atoms, constitutive oxygen, barium and cerium ions and impurities, and in particular hydrogen atoms, may be enhanced under the present irradiation conditions at elevated temperature of 473 K. The dose rate dependences of σ_{RIC} and σ_{BC} for H-undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ show the same results with that for H-doped one, although the absolute values are different.

Fig. 2(a) and (b) shows dose rate dependence of ΔRIC ($\sigma_{\Delta RIC} = \sigma_{RIC} - \sigma_{BC}$), which means the increment of the RIC, obtained by subtracting the base conductivity from the RIC, for H-doped and -undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$, respectively, in the initial and final doses during electron irradiation at 473 K. For dose rates under 200 Gy/s, the ΔRIC of H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ is about one order magnitude higher than that of H-undoped one. The difference of the ΔRIC between H-doped and -undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ may be caused by enhancement of diffusion of H due to ionizing irradiation. On the other hand, for the dose rates above 300 Gy/s, the ΔRIC of H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ was close to that of H-undoped one. The coincident of the ΔRIC indicate that the charge carrier for the conductivity is not hydrogen but constitutive atoms in the

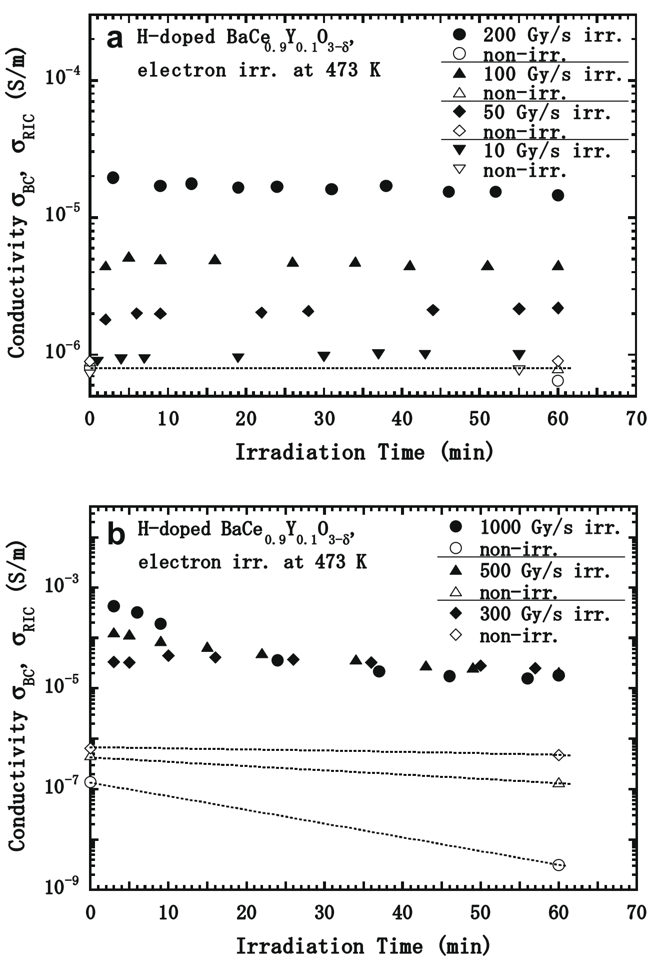

Fig. 1. Radiation induced conductivity, σ_{RIC}, of H-doped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ as a function of electron irradiation time at temperature of 473 K and ionizing dose rates of (a) 10–200 and (b) 300–1000 Gy/s, as compared with base conductivity, σ_{BC}, before and after irradiation.

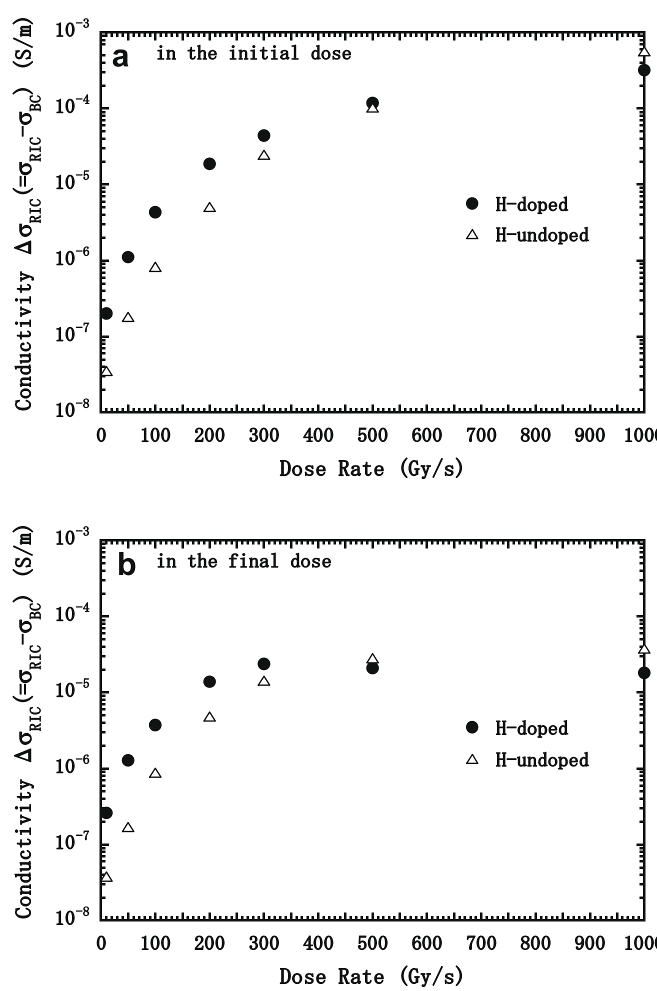

Fig. 2. Dose rate dependence of ΔRIC ($\sigma_{RIC} - \sigma_{BC}$) for H-doped and -undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ in the (a) initial and (b) final irradiation doses.

matrix, mainly oxygen. The mobility of oxygen ions in $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ generally starts at elevated temperature above 973 K [9]. The diffusion of oxygen ions may be enhanced by ionizing effects with high dose rates above 300 Gy/s even if the temperature is 473 K.

4. Summary

To investigate the role of hydrogen in the perovskite-type insulating materials under irradiation, the conductivities of the H-doped and -undoped $BaCe_{0.9}Y_{0.1}O_{3-\delta}$ were in situ measured during electron irradiation with 10–1000 Gy/s at 473 K. The conductivity in the final dose for irradiation time of 60 min increased as the dose rate increased up to 300 Gy/s, and those at 100 and 300 Gy/s became about two and three, respectively, orders of magnitude higher than the base conductivity without radiation, where it is called RIC. It was found that the RIC for the H-doped specimen was higher by one order of magnitude than that for the H-undoped one. The results may show that the RIC takes place due to hydrogen diffusion as well as electronic excitation, enhanced by ionizing effects. From 300 to 1000 Gy/s, the RIC in the final dose hardly depended on the dose rate and the hydrogen concentration. The base conductivity due to protonic conduction after irradiation was reduced to about one order of magnitude lower before one. Namely RIED was observed. The dose rate dependence of the RIC above 300 Gy/s may probably show that the ionic conductions due to constitutive oxygen elements in $BaCe_{0.9}Y_{0.1}O_{3-\delta}$, are caused by the ionizing effects, and the behavior of the excited hydrogen atoms is suppressed by them.

Acknowledgment

The authors are indebted to Mr. Francisco Javier Valle for his valuable help in the experiments.

References

[1] E.R. Hodgson, Nucl. Instrum. and Meth. B 191 (2002) 744.
[2] B. Tsuchiya, T. Shikama, S. Nagata, K. Toh, M. Narui, M. Yamazaki, J. Nucl. Mater. 367–370 (2007) 1073.
[3] G.P. Pells, J. Nucl. Mater. 155–157 (1988) 67.
[4] S.J. Zinkle, E.R. Hodgson, J. Nucl. Mater. 191–194 (1992) 58.
[5] B. Tsuchiya, A. Moroño, E.R. Hodgson, T. Shikama, J. Physica Scripta T118 (2005) 18.
[6] E.R. Hodgson, S. Clement, J. Nucl. Mater. 155–157 (2007) 1988.
[7] H. Iwahara, Solid State Ionics 77 (1995) 289.
[8] B. Tsuchiya, K. Morita, S. Nagata, K. Toh, T. Shikama, Nucl. Instrum. and Meth. B 257 (2007) 541.
[9] J. Guan, S.E. Dorris, U. Balachandran, M. Liu, Solid State Ionics 100 (1997) 42.