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Anomalous exchange of deuterium implanted into an oxide ceramic for protium in air vapor

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Abstract

This paper describes an anomalous exchange of deuterium in an oxide ceramic, $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ by protium in air-vapor. The ceramic specimen was implanted with 5 keV D_2^+ ion beam up to saturation at room temperature and exposed to normal air introduced into the vacuum chamber. It was eventually found by means of the elastic recoil detection technique that deuterium implanted was almost completely exchanged for protium which was included in the air-vapor. On the other hand, it was found in the vice versa case that no exchange of protium implanted into the ceramic for deuterium in D_2O vapor took place. The mechanism for such an anomalous isotope replacement is discussed. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Dynamic behaviors of hydrogen atoms in oxide ceramics receive intensive attention in applied point of views such as high temperature protonic conductors in electrochemical devices and tritium breeding materials in fusion devices. $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ is a typical proton conducting oxide ceramic which is perovskite-type and exhibits high protonic conductivity under hydrogen-containing atmosphere at elevated temperatures [1]. Dynamic behaviors of hydrogen in the ceramics have been studied by many authors, using various experimental techniques such as the conductivity measurement [2], luminescence spectroscopy [3], neutron diffraction [4], and ion beam analysis [5]. However, detailed properties of hydrogen atoms in the ceramics have not been well understood yet. The fundamental understanding is important for further applications.

For tritium breeding ceramic materials, important key issues concerning hydrogen behaviour are recovery of tritium produced during reactor operation and reduction of tritium inventory for maintenance. These are closely related to re-emission processes of hydrogen and isotope replacement of tritium by protium. In the present study, for more common purpose, retention and re-emission of H and D implanted into an oxide ceramic, $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$, up to saturation has been studied by means of the elastic recoil detection (ERD) technique. It has been eventually found that deuterium implanted into the ceramic is almost completely replaced by protium in normal air-vapor when the as-implanted ceramic is exposed to normal air introduced in the vacuum chamber.

In this paper, we report the experimental results on the anomalous exchange of deuterium in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ for protium in air-vapor at room temperature and on the retention of H and D in the ceramic irradiated simultaneously with 4 keV H_2^+ and 3 keV D_2^+ ions and moreover discuss the mechanism for the anomalous isotope exchange.

2. Experimental

The specimen used was a disc of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ of 10^{-2} m in diameter and 2×10^{-3} m in thickness, which was prepared by a solid state reaction and sintering process [6]. The specimen was placed on a

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manipulator in contact with a ceramic heater in a conventional UHV chamber, which was evacuated to the base pressure of 4.0×10^{-7} Pa. Prior to hydrogen ion implantation, the specimen was heated at 973 K for 10 min in order to remove out residual hydrogen (protium). The temperature was measured with a thermocouple of alumel–chromel. The specimen was implanted with 5 keV D_2^+ ions, or 5 keV H_2^+ ions at a flux of 4.0×10^{17}/m^{2}s up to saturation at room temperature. The specimens were exposed to normal air including H_2O vapor and to an atmosphere including D_2O vapor. They were also soaked in solution of H_2O, or D_2O. Before and after those treatments, the depth profiles of H and D in each specimen were measured by means of the ERD technique [7], where the recoil H^+ and D^+ ions were detected through thin foil filter at a forward recoil angle of 20° to the incident direction of 1.7 MeV He^+ ion beam which is inclined at 80° to the surface normal. The Rutherford backscattering (RBS) spectrum was measured simultaneously at an angle of 150° to the incident

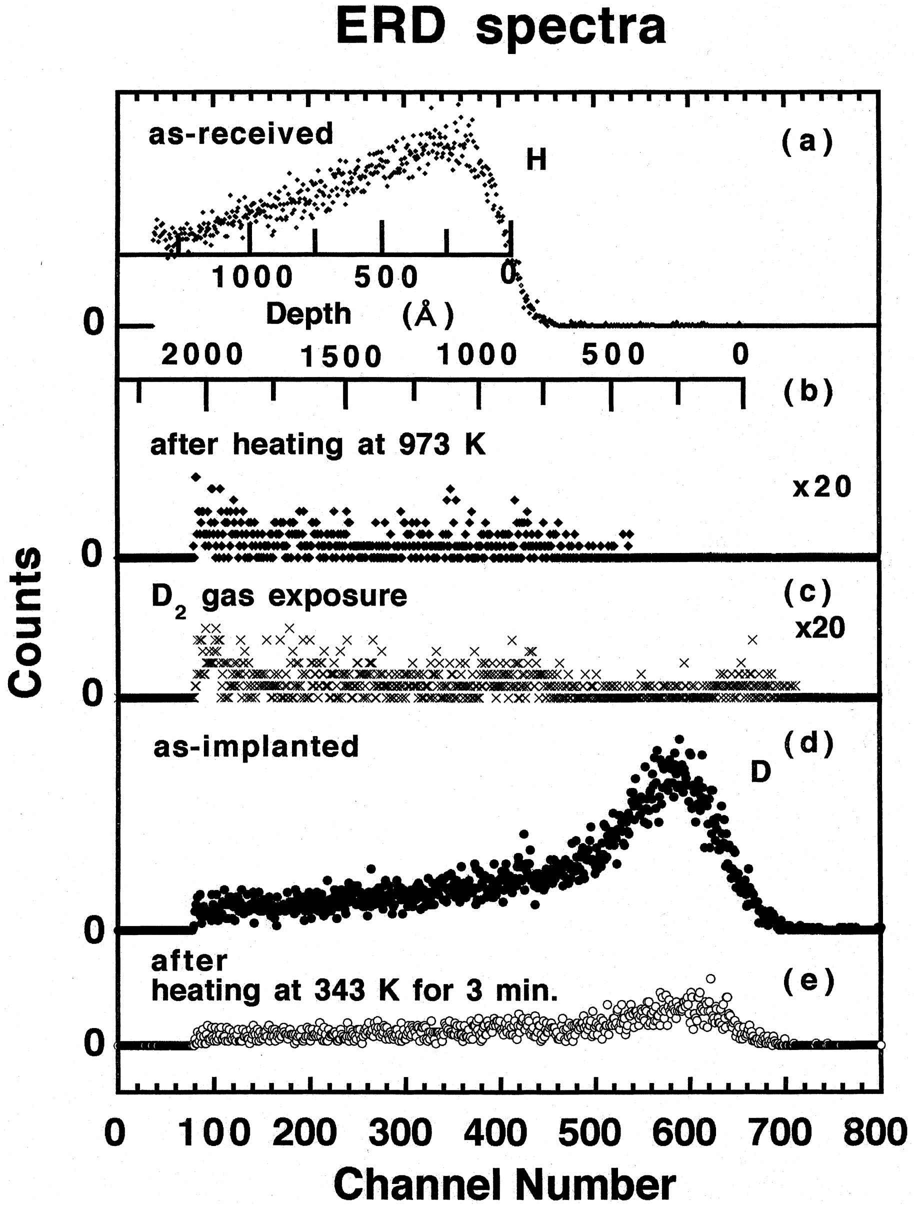

Fig. 1. ERD spectra of 1.7 MeV He^+ ion beam from the specimen as-received (a), heated at 973 K for 10 min (b), exposed to D_2 gas at 1.3×10^{-2} Pa (c), implanted up to saturation with 5 keV D_2^+ ions (d), and heated at 343 K for 3 min (e).

direction in order to monitor the fluence of 1.7 MeV He^+ ion beam.

In order to investigate the re-emission rates of H and D, the retention of H and D in the ceramic irradiated simultaneously with 4 keV H_2^+ and 3 keV D_2^+ ions was measured. In the experiment, the peak depths of H and D implanted coincided with each other.

3. Experimental results and discussion

Typical ERD spectra of 1.7 MeV He^+ ion beam from the specimen measured at each stage of the standard procedures in the present study are shown in Fig. 1, where ERD spectra obtained for the specimen as-received (a), heated at 973 K for 10 min (b), exposed to D_2 gas at 1.3×10^{-2} Pa (c), implanted 5 keV D_2^+ ions up to saturation (d) and subsequently heated at 343 K for 3 min (e), are shown, and the horizontal axis of channel number represents the kinetic energy of recoiled species. One can estimate the depths of H and D retained in the specimen from the kinetic energy of the recoiled species using the standard method which are shown in Fig. 1 (a) and (b). It is clearly seen from (a) and (b) of Fig. 1 that protium is retained in the as-received specimen and it is removed out by heating at 973 K for 10 min and it is also seen from the small peak in (c) that deuterium is retained only at the top surface by exposure of the specimen to D_2 gas at 1.3×10^{-2} Pa, which gives the zero point in the depth scale. Moreover it is seen from (d) that deuterium retained in the specimen by the ion implantation is mostly peaked at a depth of 250 Å which corresponds to the projected range of 2.5 keV D^+ ion in the specimen and from (e) that it is almost re-emitted by heating at 343 K for 3 min.

From the standard analysis of the ERD spectrum for the specimen as-implanted in (d), it was found that the ratio of the saturation concentration of D implants to the molar concentration of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ is 1.1 ± 0.1. It was also found that the fractional saturation concentration of H implants in the specimen implanted with 5 keV H_2^+ ions at room temperature is almost the same as that of D implants. The isochronal annealing experiments of the specimens implanted with 5 keV D_2^+ ions or 5 keV H_2^+ ions up to saturation indicated that the H and D implants were almost re-emitted by heating at the temperature of around 363 K for 10 min.

The ERD spectra for the specimen only heated at 973 K for 10 min and subsequently exposed to normal air for

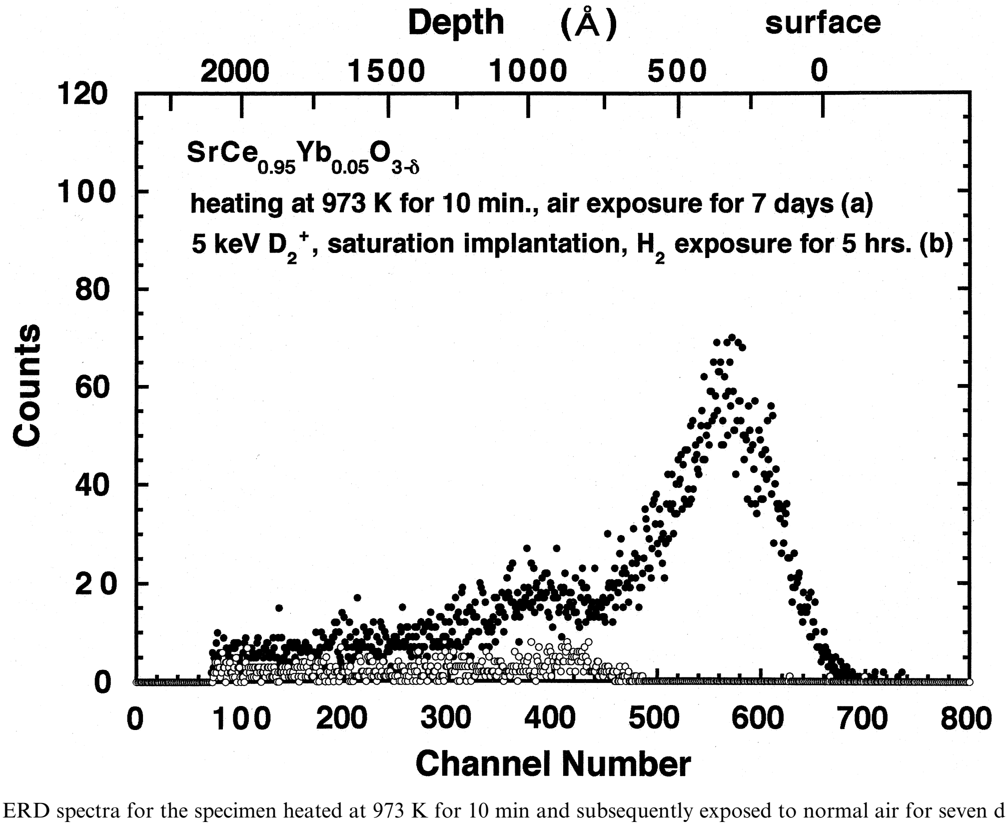

Fig. 2. The ERD spectra for the specimen heated at 973 K for 10 min and subsequently exposed to normal air for seven days (a) and implanted with 5 keV D_2^+ ions up to saturation at room temperature and subsequently exposed to H_2 gas for 5 h at 1.3×10^{-2} Pa (b).

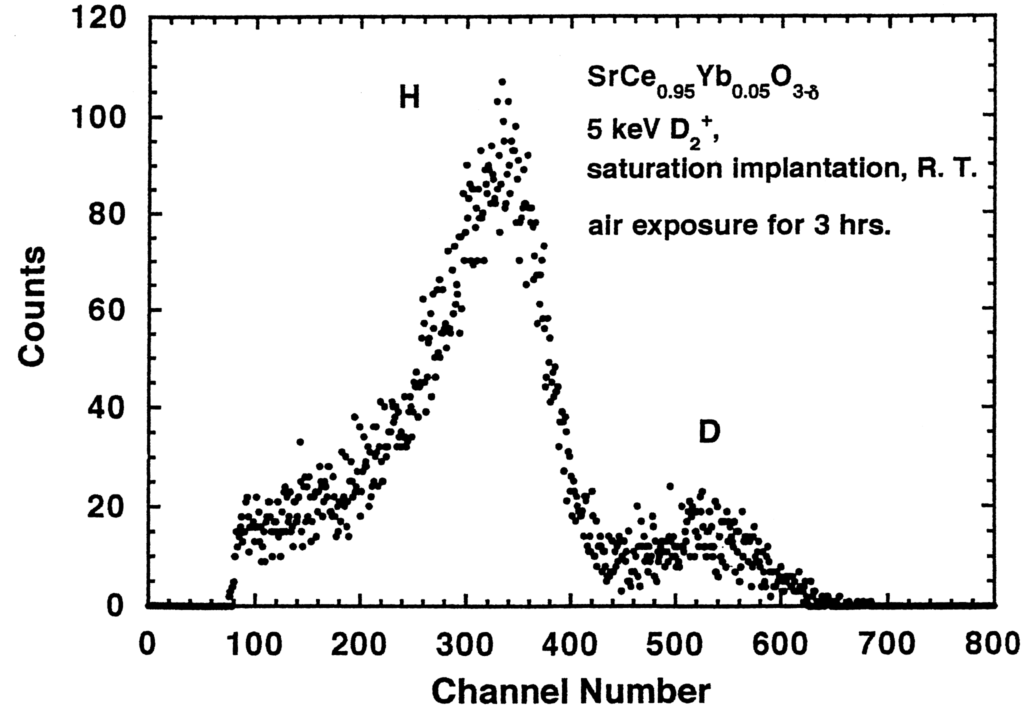

Fig. 3. The ERD spectra for the specimen implanted with 5 keV D_2^+ ions up to saturation and subsequently exposed to normal air for 3 h in the chamber at room temperature.

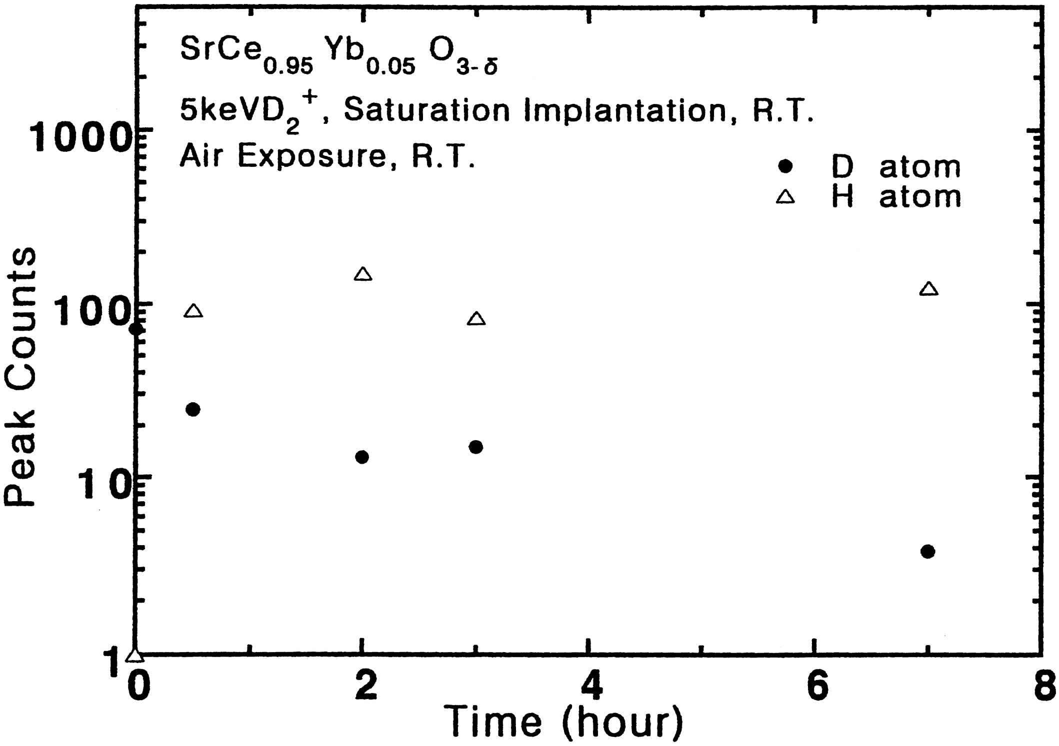

Fig. 4. Time-variation of the retained number of D implanted up to saturation at room temperature and of the uptake number of H in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ exposed to normal air in the chamber.

seven days in the chamber and implanted with 5 keV D_2^+ ions up to saturation at room temperature and subsequently exposed to H_2 gas for 5 h at 1.3×10^{-2} Pa are shown in Fig. 2(a) and (b), respectively, and the ERD spectrum for the specimen implanted 5 keV D_2^+ ions up to saturation and subsequently exposed to normal air for 3 h in the chamber at room temperature is shown in Fig. 3. It is seen from Figs. 2(b) and 3 that D implants are not exchanged for H atoms by the exposure to H_2 gas, but are almost exchanged for H atoms by the exposure to normal air. It is also seen from Fig. 2(a) that H atoms are not taken in the ceramic specimen with no D implants by the exposure of normal air.

The exchange behavior of D implants for H atoms by exposure to normal air is shown as a function of exposure time in Fig. 4. It is clearly seen from Fig. 4 that the air exposure for 7 h exchanges completely D implants for H atoms.

The vice versa experiments were done in order to understand the anomalous isotope exchange in details. The ERD spectra from the specimen as implanted with 5 keV H_2^+ ions up to saturation at room temperature (○) and subsequently exposed to an atmosphere of D_2O vapor for 3 days (●) are shown in Fig. 5. It is clearly seen from Fig. 5 that D atoms are not taken in the specimen at all by exposure to the atmosphere of D_2O vapor even for 3 days although H implants are a little bits reduced. Furthermore, in order to confirm such an anomalous isotope exchange, the specimen implanted with 5 keV D_2^+ ions up to saturation was soaked into H_2O water and vice versa. The ERD spectra for both cases are shown in Fig. 6(a) and (b). It is also seen from Fig. 6, as shown above, that D implants are completely replaced by H atoms, while H implants are not replaced at all.

The experimental results described above are concluded to indicate that the exchange of D implants for H atoms in H_2O vapor takes place in the following steps: dissociative adsorption of O–H species at the specimen surface, diffusion of H, and re-emission of D due to formation of HD and trapping of H into vacant trap sites which have been occupied by D. It is of essential importance to know which step produces such isotope difference. For this purpose the retention of H and D in the specimen simultaneously irradiated with 4 keV H_2^+ and 3 keV D_2^+ ions at the same flux has been measured. The retained numbers of H and D are plotted as a function of time in Fig. 7. It is seen from Fig. 7 that the

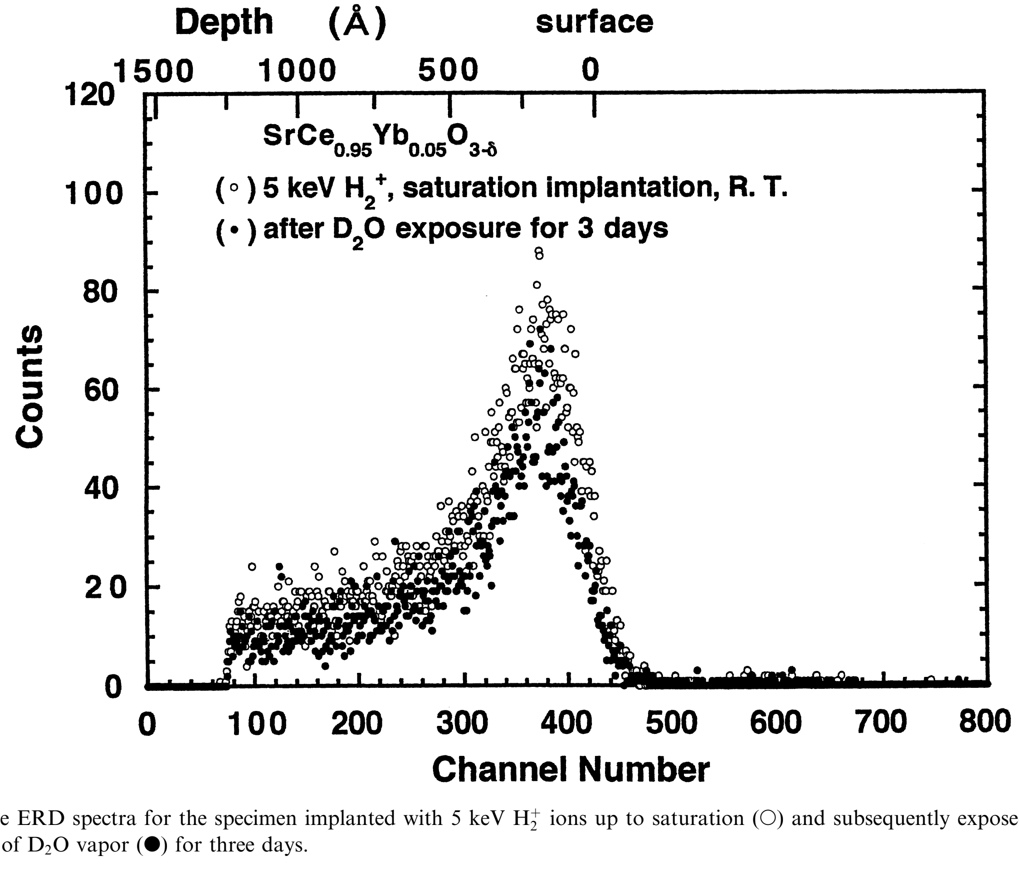

Fig. 5. The ERD spectra for the specimen implanted with 5 keV H_2^+ ions up to saturation (○) and subsequently exposed to an atmosphere of D_2O vapor (●) for three days.

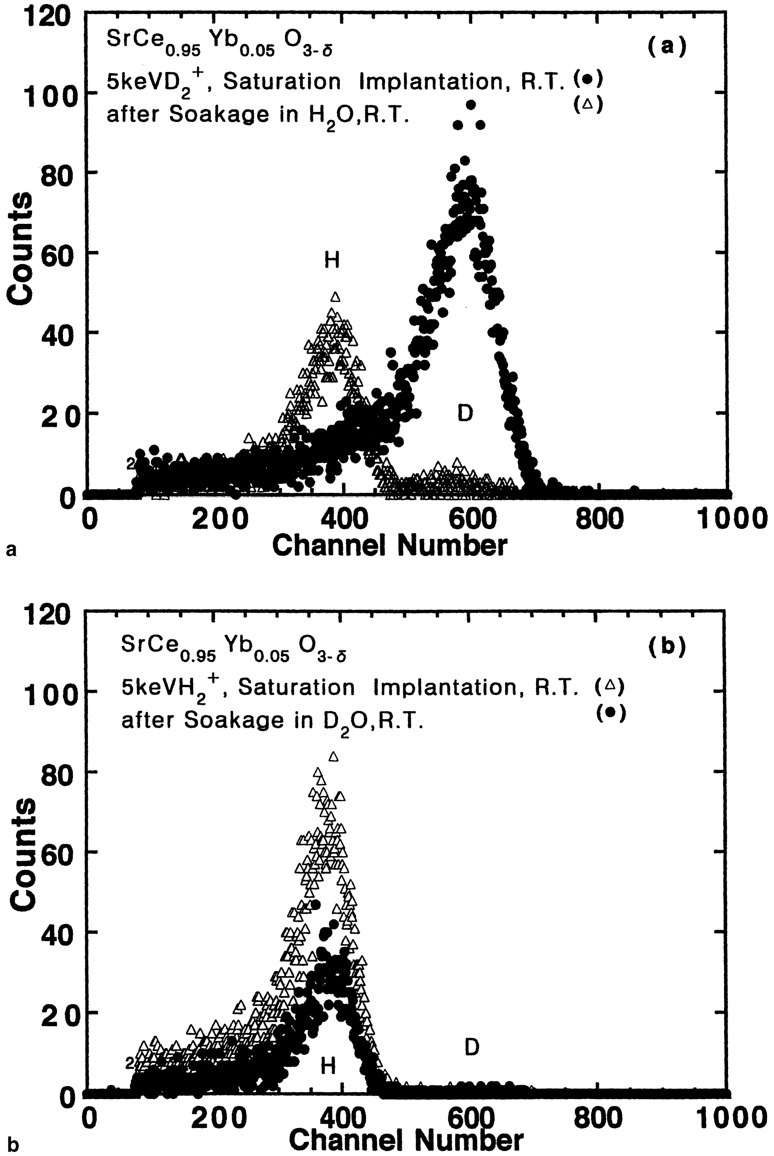

Fig. 6. The ERD spectra for the specimen implanted with 5 keV D_2^+ ions up to saturation and soaked in H_2O water (a) and with 5 keV H_2^+ ions up to saturation and soaked in D_2O water (b).

retained numbers of H and D increase in a same way in the beginning of the irradiation and hereafter the retained numbers of H and D saturate after 200 min as the irradiation time increases and the D/H ratio at saturation is about 1.3.

The saturation ratio of D/H in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ is consistent with that in Be [8]. The latter value also shows good agreement with the theoretical one which has been calculated using the mass balance equations including the elementary processes: ion-induced detrapping, retrapping and local molecular recombination between movable species. The saturation ratio of D/H ≅ 1.3 in Fig. 7 indicates that the re-emission rate of H is larger than that of D. These facts indicate that H atoms taking in the specimen take out the D implants due to formation of HD through the local molecular recombination. Therefore, one may conclude that the extreme large difference in the isotope exchange observed in the present study is attributed to the isotope difference in the dissociative adsorption process at the surface, or/and the diffusion process. In this moment, it is not clear yet which process plays major role in the anomalous isotope exchange of D implants for H atoms in air-vapor.

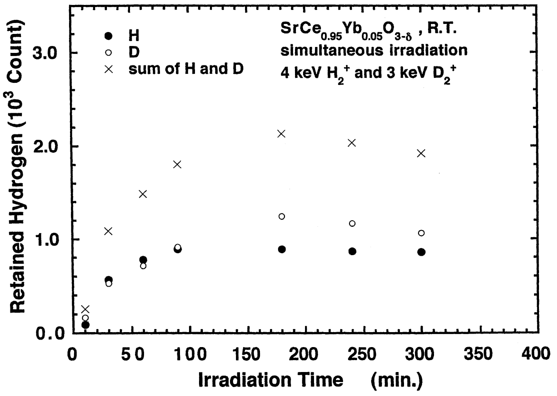

Fig. 7. Time variation of the numbers of H and D retained in $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ irradiated simultaneously at room temperature with 4 keV H_2^+ and 3 keV D_2^+ ions at the same flux.

Finally it is noted that the concept of such an anomalous isotope exchange among hydrogen species may be very effective to reduce the tritium inventory in the tritium breeding oxide ceramic material, although $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ itself is not fusion reactor materials. It is very interesting to investigate hydrogen isotopes replacement in Li-containing oxide ceramics.

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References

[1] H. Iwahara, Solid State Ionics 77 (1995) 289; 86–88 (1996) 9.
[2] S. Shin, H. Huang, M. Ishigame, H. Iwahara, Solid State Ionics 40&41 (1990) 910.
[3] Y. Yugami, S. Matsuo, M. Ishigame, Solid State Ionics 77 (1995) 195.
[4] N. Sata, K. Hiramoto, M. Ishigame, S. Hosoya, N. Niimura, S. Shin, Phys. Rev. B 54 (1996) 15795.
[5] N. Matsunami, T. Yajima, H. Iwahara, Nucl. Instr. and Meth. B 65 (1992) 278.
[6] H. Uchida, H. Yoshihara, T. Esaka, S. Ohisu, H. Iwahara, Solid State Ionics 36 (1989) 359.
[7] B. Tsuchiya, K. Morita, J. Nucl. Mater. 227 (1996) 195.
[8] B. Tsuchiya, K. Morita, J. Nucl. Mater. 241–243 (1997) 1065.