

Observation of the microstructural changes in lithium titanate by multi-ion irradiation

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Abstract

The irradiation behavior of Li_2TiO_3 under a fusion reactor environment was simulated by simultaneous irradiation of Li_2TiO_3 by the triple ion beams and the respective single ion beams of O^{2+} , He^+ and H^+ . The microstructural changes in Li_2TiO_3 caused by the irradiation were measured by Raman spectroscopy and FT-IR photoacoustic spectroscopy. The results suggest that the formation of TiO_2 due to displacements by irradiation occurs, and the irradiation defects generated by irradiation trap hydrogen and increase the amount of hydroxyl near the surface. Such phenomena are believed to significantly affect the chemical form of the released tritium and the tritium inventory in the breeding materials of a fusion reactor.

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1. Introduction

The Li_2TiO_3 ceramic is one of the most suitable candidate solid breeder materials for D–T fusion reactors because of its low activation, excellent tritium migration and chemical stability [1–3]. In the fusion reactor environment irradiation damage will be caused by fast neutrons, energetic tritons (2.7 MeV) and helium ions (2.1 MeV) generated in ${}^6\text{Li}(n,\alpha){}^3\text{H}$ reaction. The irradiation damage will result in microstructural changes that may affect the characteristics of the breeding materials, especially the tritium release behavior [4]. Thus the study of irradiation defects and microstructural changes caused by irradiation of Li_2TiO_3 is needed to evaluate its performance in a fusion reactor blanket.

Simulation of the fusion reactor environment and hence the study of any synergistic effects of atomic displacement damage in Li_2TiO_3 are could be achieved with simultaneous irradiation with ‘triple’ ion beams, which

consist of O^{2+} , He^+ and H^+ . In a previous study, the formation of the TiO_2 (anatase) layer on the surface of Li_2TiO_3 by the triple ion beam irradiation was identified by Raman spectroscopy and XRD analysis [5]. In the present study, irradiation damage and microstructural changes in Li_2TiO_3 irradiated with the triple ion beam and the respective single ion beams were examined with Raman spectroscopy and FT-IR photoacoustic spectroscopy.

2. Experimental

Li_2TiO_3 ceramics used in this experiment were fabricated from 99% pure powder purchased from CERAC, Inc. The powder was cold pressed at 300 MPa into cylinders, and subsequently sintered at 1223 K for 6 h in an Ar atmosphere. The resulting Li_2TiO_3 ceramics have approximately 78% theoretical density. The specimens were machined from the cylinders in the form of disks with diameter of 10 mm and thickness of 0.5–1 mm.

The Li_2TiO_3 samples were irradiated at 573 K with the triple ion beams and with single ion beams of 2.4 MeV O^{2+} , 0.6 MeV He^+ and 0.25 MeV H^+ in the triple

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beam irradiation facility in Takasaki laboratory of Japan Atomic Energy Research Institute [6]. The fluence of each ion type was estimated to be about $0.5\text{--}1 \times 10^{21}$ ions/m². The ion energies were determined by estimation with the TRIM code [7] to adjust the projected ranges of each species at about 2 μm .

3. Results and discussion

3.1. Raman spectroscopy

In the previous study, the formation of a TiO₂ layer on the surface of Li₂TiO₃ by the triple ion beam irradiation was identified by Raman spectroscopy [5]. In the present study, the existence of a TiO₂ layer on the surface of Li₂TiO₃ by each single ion beam irradiation has been evaluated by the Raman spectroscopy to investigate the effects of ion species on the formation of the TiO₂ layer. The Raman spectra of irradiated Li₂TiO₃ samples for each single ion beam are displayed in Fig. 1. In comparison with the reference spectra of Li₂TiO₃ and TiO₂ shown in Ref. [5], it can be seen that the Raman spectra of Li₂TiO₃ samples irradiated with the single H⁺ ion beam and the single He⁺ ion beam are quite similar to the spectrum of Li₂TiO₃. However, the spectrum of the sample irradiated with the single O²⁺ ion beam seems to be a superposition of the spectra of Li₂TiO₃ and TiO₂. It suggests that the formation of TiO₂ on the surface of Li₂TiO₃ observed in the sample irradiated with triple ion beams [5] is mainly caused by the effect of the O²⁺ ion beam irradiation.

3.2. FT-IR photoacoustic spectroscopy

As mentioned in Section 2, the projected ion ranges are estimated to be about 2 μm . It should be noted that the information about the ion ranges is not reflected in the results of Raman spectroscopy shown in Section 3.1 because the spectroscopy can obtain information about only a few layer close to the surface. Using the FT-IR photoacoustic spectroscopy (PAS) technique the non-irradiated sample, on samples irradiated with the triple ion beam and on samples irradiated by the single ion beams were examined in order to obtain a information near the end of the ion range. The photoacoustic signal was generated from the surface layers of sample with a thickness of some micrometers, which is a function of the mirror velocity of the FT-IR interferometer and wave number. In this case, the mirror velocity was 2 cm/s which corresponds to the thickness of about 15–5 μm for 400–4000 cm⁻¹, so that the spectra of irradiated samples is a superposition of spectra of irradiated and non-irradiated zones of the sample.

The FT-IR PAS spectrum of a non-irradiated sample is shown in Fig. 2. The characteristic peaks in FT-IR PAS

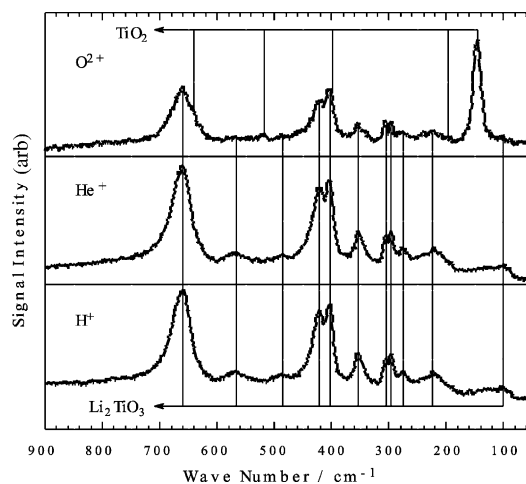


Fig. 1. Raman spectra of Li₂TiO₃ samples irradiated with single ion beams of O²⁺, He⁺, and H⁺. Peaks from Li₂TiO₃ and TiO₂ layers are indicated.

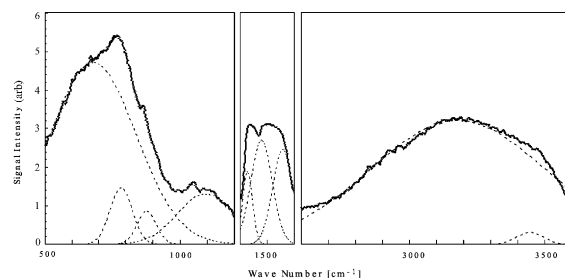


Fig. 2. FT-IR PAS spectrum of non-irradiated Li₂TiO₃ sample. Dashed lines are the results of peak analysis.

spectra were observed around 680, 780, 880, 1090, 1430, 1480, 1570, 3150, 3450 cm⁻¹. The 880, 1090, 1430 and 1490 cm⁻¹ peaks are believed to be due to Li₂CO₃ which is one of the raw materials of Li₂TiO₃ samples and is believed to exist as an impurity in the samples [8]. In comparison to the reported spectra of TiO₂ and Li₂TiO₃, 680 and 780 cm⁻¹ peaks are identified as due to Ti–O, and 1570, 3150 and 3450 cm⁻¹ peaks are from the O–H bond in hydroxyls adsorbed on or near the surface [9–11].

Among the observed peaks, irradiation effect is clearly found for 780 and 3450 cm⁻¹ peaks. Fig. 3 shows the relation between the average displacements per atom (dpa) in the depth measurable with FT-IR PAS and the increase of 780 cm⁻¹ peak area from the Ti–O bond, for each irradiation. The dpa was estimated with the TRIM code. It is shown that the peak area increase is proportional to the average dpa. To simulate the formation of TiO₂ in Li₂TiO₃, Li₂TiO₃ samples doped with 1–10% TiO₂ were prepared. Fig. 4 shows the relation between the ratio of doped TiO₂ and the increase of 780 cm⁻¹ peak area. It is also shown that the peak area increases in proportion to the ratio of doped TiO₂. From the

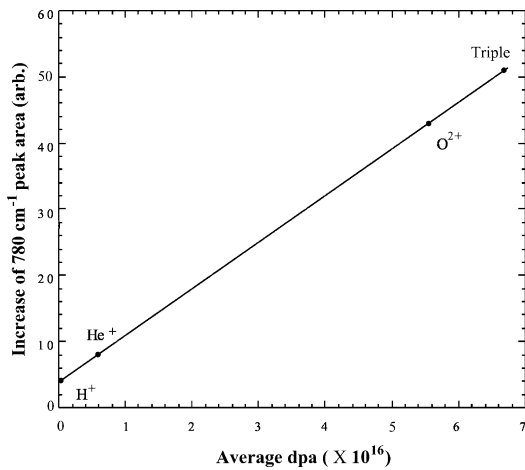


Fig. 3. Dependence of the increase of 780 cm⁻¹ peak area on the average dpa.

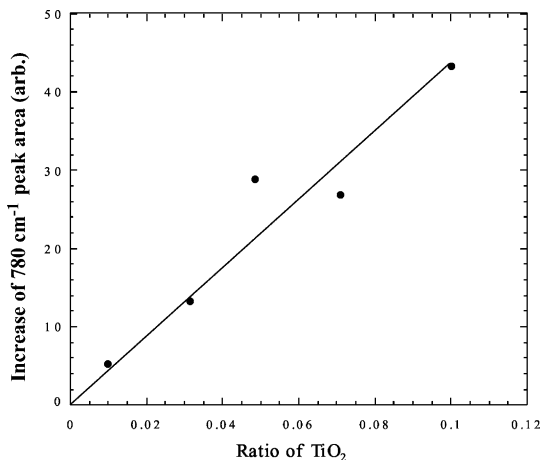


Fig. 4. Dependence of the increase of 780 cm⁻¹ peak area on the ratio of doped TiO₂.

comparison of the results in Figs. 3 and 4, it is suggested that TiO₂ observed by Raman spectroscopy in the sample irradiated with the triple ion beams is formed by displacements, and the amount of TiO₂ is proportional to the dpa in the sample. Although the formation of TiO₂ is not observed with Raman spectroscopy in the samples irradiated with the single H⁺ and the single He⁺ ion beam, the results of FT-IR PAS suggest that TiO₂ is also formed in these samples. The average dpa in the measurable depth with FT-IR PAS in the sample irradiated with the single O²⁺ ion beam is estimated to be about 10 times larger than that in the sample irradiated with the single He⁺ ion beam and about 100 times larger than that in the sample irradiated with the single H⁺ ion beam. However, at the region nearest the surface, the dpa difference among the samples irradiated with the respective single ion beams is estimated to be much

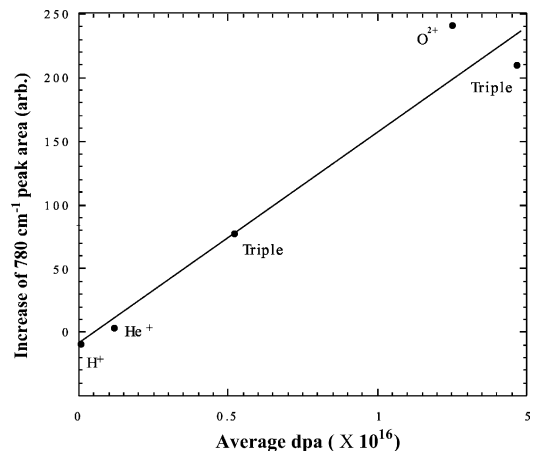


Fig. 5. Dependence of the increase of 3450 cm⁻¹ peak area on the average dpa.

larger. For example, at the depth of 40 nm, the dpa in the samples irradiated with the single O²⁺, the single He⁺ and the single H⁺ ion beam is calculated to be about 1.1, 0.02 and 0.004, respectively. This large difference in dpa is believed to be the reason the formation of TiO₂ in the samples irradiated with the single He⁺ and the single H⁺ ion beam cannot be observed with Raman spectroscopy. In the previous study, it was found that the formation of TiO₂ is promoted by increase of the irradiation temperature [5]. Since the irradiation temperature in this study, 573 K, is much lower than the operation temperature of fusion reactor blanket, it is expected that the amount of TiO₂ formed in the blanket is larger than that observed in this study.

Fig. 5 shows the relation between the average dpa in the measurable depth with FT-IR PAS and the increase of 3450 cm⁻¹ peak area, which is due to the O–H bond. The peak area increases in proportion to the average dpa. In this case, there is no relation between the increase of 3450 cm⁻¹ peak area and the amount of doped TiO₂. Thus, it suggests that the increase of 3450 cm⁻¹ peak area observed in the irradiation samples has no relation to the formation of TiO₂ by irradiation, and the defects generated by displacements become the trapping sites for hydrogen adsorbed on or near the surface, so that the amount of hydroxyl near the surface increased proportionally to the dpa. It must be noted that such the hydrogen-trapping sites would also trap tritium generated in the fusion environment and would disturb the rapid recovery of tritium from the breeding material.

4. Conclusions

The microstructural changes in Li₂TiO₃ irradiated with the triple ion beam and with single ion beams of H⁺, He⁺ and O²⁺ were observed by Raman spectroscopy and

FT-IR PAS. The results of Raman spectroscopy suggest that the formation of the TiO₂ layer observed in the sample irradiated with the triple ion beams is mainly caused by the effect of the O²⁺ ion irradiation. The results of FT-IR PAS also suggest that amount of TiO₂ formed is proportional to the average dpa, and that the defects generated by irradiation would trap hydrogen near the surface. The formation of TiO₂ and increase in the amount of hydroxyl near the surface observed in this study are believed to significantly affect the chemical form of released tritium and the tritium inventory in the breeding material of a fusion reactor. Further study of the effects of dpa on the tritium release is needed. The effects of ion species and simultaneous irradiation on microstructural changes were not observed in this study. It is necessary to verify such effects by further experiment such as irradiation to the same dpa with different ion species.

References

- [1] N. Roux, J. Avon, A. Floreancig, J. Mougin, B. Rasneur, S. Ravel, *J. Nucl. Mater.* 233–237 (1996) 1431.
- [2] P. Gierszewski, H. Hamilton, J. Miller, J. Sullivan, R. Verrall, J. Earnshaw, D. Ruth, R. Macauley-Newcombe, G. Williams, *Fus. Eng. Des.* 27 (1995) 297.
- [3] T. Tanifuji, D. Yamaki, S. Nasu, K. Noda, *J. Nucl. Mater.* 258–263 (1993) 543.
- [4] T. Tanifuji, D. Yamaki, K. Noda, O.D. Slagle, F.D. Hobbs, G.W. Hollenberg, in: *Proceedings of the 19th Symposium on Fusion Technology*, 1996, p. 1455.
- [5] T. Nakazawa, V. Grishmanovs, D. Yamaki, Y. Katano, T. Aruga, A. Iwamoto, in: *Proceedings of the 2000 International Conference on Ion Implantation Technology*, 2000, p. 753.
- [6] S. Hamada, Y. Miwa, D. Yamaki, Y. Katano, T. Nakazawa, K. Noda, *J. Nucl. Mater.* 258–263 (1998) 383.
- [7] J.F. Ziegler, J.P. Biersack, U. Littmark, *The Stopping and Range of Ions in Solids*, Pergamon, Oxford, 1985.
- [8] S. Oohira, M. Kakihana, Y. Fujii, T. Nagumo, M. Okamoto, *J. Nucl. Mater.* 131&134 (1985) 201.
- [9] G. Durinck, H. Poelman, P. Clauws, L. Fiermans, J. Vennik, G. Dalmai, *Solid State Commun.* 80 (1991) 579.
- [10] K. Morishige, F. Kanno, S. Ogiwara, S. Sasaki, *J. Phys. Chem.* 89 (1985) 4404.
- [11] S. Tanaka, M. Taniguchi, M. Nakatani, D. Yamaki, M. Yamawaki, *J. Nucl. Mater.* 218 (1995) 335.