



# XPS analysis on chemical states of $\text{Li}_4\text{SiO}_4$ irradiated by 3 keV $\text{D}_2^+$

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## ABSTRACT

$\text{Li}_4\text{SiO}_4$  will be applied as tritium breeding materials in future fusion reactor. The release behavior of tritium from neutron-irradiated  $\text{Li}_4\text{SiO}_4$  should be sensitive to the chemical states of lithium, oxygen and silicon on the surface of  $\text{Li}_4\text{SiO}_4$  with irradiated defects. The present study is focused on the influence of hydrogen isotopes and irradiation defects on surface chemical state of  $\text{Li}_4\text{SiO}_4$ . The X-ray Photoelectron Spectroscopy (XPS) was compared between non-irradiated  $\text{Li}_4\text{SiO}_4$  and  $\text{D}_2^+$ -irradiated one. It was observed by that the binding energy (BE) of electron for Li-1s, O-1s and Si-2p of non-irradiated  $\text{Li}_4\text{SiO}_4$  were 60.9 eV, 536.1 eV and 107.1 eV respectively. However new XPS peak for Li-1s at 57.2 eV, three XPS peaks for O-1s (at 536.1 eV, 533.2 eV and 531.3 eV, respectively) and three XPS peaks for Si-2p (at 107.1 eV, 104.2 eV and 99.7 eV, respectively) were observed in  $\text{D}_2^+$ -irradiated  $\text{Li}_4\text{SiO}_4$ . It is considered that the XPS peaks of 531.3 eV and 104.2 eV should be corresponding to O-1s and Si-2p in  $-\text{Si}-\text{O}-\text{D}$  while the XPS peak of 533.2 eV should be corresponding to O-1s in  $\text{D}-\text{O}-\text{D}$ . The formation of  $-\text{Si}-\text{O}-\text{D}$  and  $\text{D}-\text{O}-\text{D}$  is considered to be due to typical irradiated defects (lithium vacancy, silicon vacancy and implanted deuterium) induced by  $\text{D}_2^+$ -irradiation.

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## 1. Introduction

In ITER test blanket module design, the elucidation of tritium recovery from solid tritium breeding material is one of critical issues for TBM design. The study of hydrogen isotopes behavior in solid breeding materials is one of the most important subjects in the design of test blanket module. There are a variety of ternary lithium oxides such as  $\text{Li}_4\text{SiO}_4$  and  $\text{Li}_2\text{TiO}_3$  that could be employed as a candidate solid breeding materials for D–T fusion reactor. Okuno et al. [1–4], Oya et al. [5–7] and Tanaka et al. [8–13] have carried out some studies on behaviors of hydrogen isotopes in these ternary lithium oxides.  $\text{Li}_4\text{SiO}_4$  will be applied as tritium breeding materials in EU helium cooled pebble blanket (HCPB) and CN helium cooled solid blanket (HCSB). Tritium should be released as HTO or HT from surface of  $\text{Li}_4\text{SiO}_4$  after neutron irradiation. And the ratio of tritium released as HTO to HT is one of key parameters for establishment of tritium extraction system in fusion reactor. The release chemical form of tritium should be determined by surface chemical environment of  $\text{Li}_4\text{SiO}_4$  affected by various radiation defects.

The typical irradiation defects induced by neutron irradiation in  $\text{Li}_4\text{SiO}_4$  are considered to consist of Li vacancy, Si vacancy and F-centers (oxygen vacancy with one or two electrons). The formation of Li vacancies is considered to be mainly due to the breeding reaction between neutron and lithium. And the displacements induced by neutrons irradiation or/and products of breeding reaction

such as helium and tritium ions with high energy of about 2 MeV can provide Si vacancies, F-centers and some Li vacancies. Tritium produced by breeding reactions in  $\text{Li}_4\text{SiO}_4$  can be located at Li vacancy to turn into the substitutional  $\text{T}^+$  for  $\text{Li}^+$  (sub.  $\text{T}_{\text{Li}}^+$ ) and at Si vacancy to the substitutional  $\text{T}^+$  for Si (sub.  $\text{T}_{\text{Si}}^+$ ). Tritium can also be located at an interstitial site to turn into the interstitial  $\text{T}^+$  (int.  $\text{T}^+$ ). Therefore there are three possible states of  $\text{T}^+$  in  $\text{Li}_4\text{SiO}_4$  after neutron irradiation, namely sub.  $\text{T}_{\text{Li}}^+$ , sub.  $\text{T}_{\text{Si}}^+$  and int.  $\text{T}^+$ . All of  $\text{T}^+$  (whether sub.  $\text{T}^+$  or int.  $\text{T}^+$ ) will be attracted by neighboring oxygen ions to form the  $-\text{OT}^-$  of sub.  $\text{T}^+$  or int.  $\text{T}^+$  [1–4,12,13].

However the experiments of neutron irradiation or tritium ions irradiation are difficult to be performed. Hence the  $\text{D}_2^+$ -irradiation has been applied as a technique of hydrogen isotopes implantation. It is considered that the displacements or sputtering by  $\text{D}_2^+$ -irradiation can provide Li vacancies, Si vacancies, and F-centers.  $\text{D}_2^+$ -irradiation can also induce the deuterium as sub.  $\text{D}_{\text{Li}}^+$ , sub.  $\text{D}_{\text{Si}}^+$  and int.  $\text{D}^+$  which is similar to the case of tritium in neutron irradiation. All of  $\text{D}^+$  (whether sub.  $\text{D}^+$  or int.  $\text{D}^+$ ) will be attracted by neighboring oxygen ions to form the  $-\text{OD}^-$  of sub.  $\text{D}^+$  or int.  $\text{D}^+$  [8–13].

Some surface analysis methods combined with deuterium implantation technical have contributed to the study on release behavior of hydrogen isotopes from various ternary lithium oxides affected by irradiation defects [1–13]. It has been observed that deuterium implanted into  $\text{Li}_4\text{SiO}_4$  can be desorbed as hydrogen molecular forms ( $\text{D}_2/\text{HD}$ ) and water forms ( $\text{D}_2\text{O}/\text{HDO}$ ), which is corresponding to that tritium produced in neutron-irradiated  $\text{Li}_4\text{SiO}_4$  can be released as HT and HTO. From the viewpoint of tritium extraction system, desorption of tritium as hydrogen molecular forms means higher safety and efficiency than that as water forms.

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Desorption of hydrogen isotopes as water forms and/or hydrogen molecular forms might be due to the existence states of hydrogen isotopes on the surface of irradiated  $\text{Li}_4\text{SiO}_4$ . However it is difficult to observe the existence states of hydrogen isotopes directly. To analyze the existence states of hydrogen isotopes indirectly, the present study was focused on the chemical states of other elements such as Li, O and Si on the surface of  $\text{Li}_4\text{SiO}_4$  affected by hydrogen isotopes and irradiation defects. Deuterium ion implantation (3 keV  $\text{D}_2^+$ -irradiation) was used to induce hydrogen isotopes (deuterium instead of tritium) and other irradiation defects into the surface of  $\text{Li}_4\text{SiO}_4$ . The chemical states of lithium (Li-1s), oxygen (O-1s) and silicon (Si-2p) were checked by X-ray Photoelectron Spectroscopy (XPS) before and after  $\text{D}_2^+$ -irradiation respectively.

## 2. Experimental

### 2.1. Material

The  $\text{Li}_4\text{SiO}_4$  powder prepared by solid reaction method in Southwestern Institute of Physics (SWIP) (total content of impurity elements <0.1%, monoclinic phase purity of  $\text{Li}_4\text{SiO}_4$  > 98%) was sintered to a plate with the diameter of about 10 mm and the thickness of about 1 mm in Shizuoka University.

### 2.2. Experimental methods

The apparatus in Shizuoka University consists of two vacuum chambers connected to each other via a gate valve and one sample-loading chamber. One vacuum chamber (signed as T-chamber) is equipped with heating system, Quadrupole Mass Spectrometer (QMS) and ion guns, and the other (signed as X-chamber) is with X-ray Photoelectron Spectroscopy (XPS) ESCA 5800 manufactured by ULVAC PHI Inc. Both T-chamber and X-chamber are evacuated to less than  $10^{-8}$  Pa using ion pumps. The  $\text{K}\alpha$  of Al was used for X-ray source.

Firstly the sintered  $\text{Li}_4\text{SiO}_4$  plate was sent to T-chamber by the one sample-loading chamber. Before  $\text{D}_2^+$ -irradiation the preheating treatment for  $\text{Li}_4\text{SiO}_4$  plate was performed at 1000 K for 3 h in T-chamber to remove volatile compounds impurities in the sample. When the sample was cooled down to room temperature (R.T. about 300 K), it was sent to X-chamber by sample-loading chamber. The Li-1s, Si-2p and O-1s XPS spectra on the surface of original  $\text{Li}_4\text{SiO}_4$  plate were obtained as the basis of comparison.

Secondly the sample was sent back to T-chamber and 3 keV  $\text{D}_2^+$ -irradiation with the fluence of  $1.0 \times 10^{22} \text{ D}^+ \text{ m}^{-2}$  and the flux of  $2 \times 10^{18} \text{ D}^+ \text{ m}^{-2} \text{ s}^{-1}$  was conducted to the sample. The ion implantation depth of the corresponding 1.5 keV  $\text{D}^+$  was about 50 nm according to calculation by SRIM2003 code, which is sufficient for XPS. After irradiation the sample was sent to into X-chamber and the Li-1s, Si-2p and O-1s XPS spectra on the surface of  $\text{D}_2^+$ -irradiated  $\text{Li}_4\text{SiO}_4$  plate were checked respectively.

Thirdly the sample was sent back to T-chamber to be heated to 1000 K with the heating rate of 5 K/min and kept at 1000 K until no deuterium is released from the sample, which is called as heating recovery process. During heating recovery process thermal desorption spectroscopy (TDS) of deuterium from irradiated  $\text{Li}_4\text{SiO}_4$  was observed by QMS. After the sample was cooling down to R.T. in vacuum, it was sent into X-chamber and the Li-1s, Si-2p and O-1s XPS spectra on the surface of  $\text{Li}_4\text{SiO}_4$  were checked respectively again.

## 3. Results

The Li-1s XPS spectra of  $\text{Li}_4\text{SiO}_4$  before  $\text{D}_2^+$ -irradiation, after  $\text{D}_2^+$ -irradiation and after heating recovery process are compared in

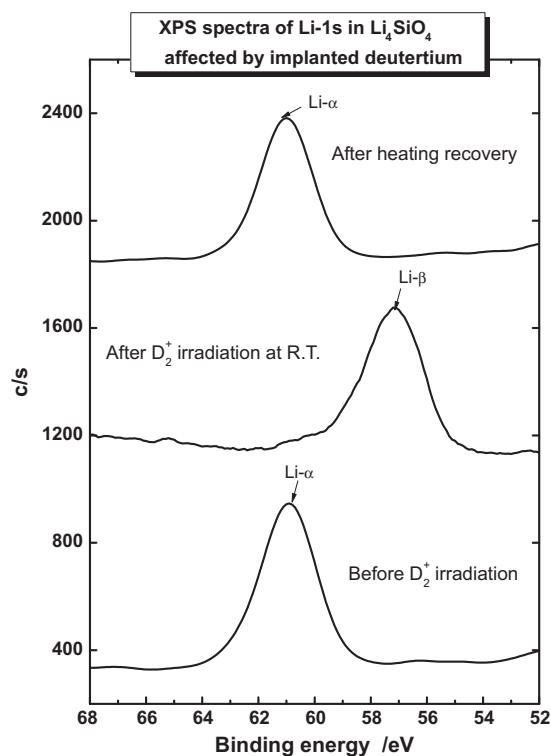


Fig. 1. XPS spectra of Li-1s in  $\text{Li}_4\text{SiO}_4$ .

Fig. 1. The binding energy of electron (BE) for Li-1s is mainly observed at 60.9 eV before  $\text{D}_2^+$ -irradiation. And that is shifted to 57.2 eV after 3 keV  $\text{D}_2^+$ -irradiation at R.T. and shifted back to 60.9 eV after TDS. The shifting of BE for Li-1s is considered to be due to the change of chemical state of lithium on the surface of  $\text{Li}_4\text{SiO}_4$  by  $\text{D}_2^+$ -irradiation. For convenience the XPS peak for Li-1s at 60.9 eV is labeled as Li- $\alpha$  and that at 57.2 eV as Li- $\beta$ .

The O-1s XPS spectra of  $\text{Li}_4\text{SiO}_4$  before  $\text{D}_2^+$ -irradiation, after  $\text{D}_2^+$ -irradiation and after heating recovery process are compared in Fig. 2. The binding energy of electron (BE) for O-1s is mainly observed at 536.1 eV before  $\text{D}_2^+$ -irradiation. And multiple XPS peaks for O-1s are observed at the range of 530–540 eV after 3 keV  $\text{D}_2^+$ -irradiation at R.T. It is considered that the XPS spectra of O-1s after irradiation consist of three XPS peaks, namely, the first is at 536.1 eV, the second is at 533.2 eV, and the third is at 531.3 eV. It is also observed that the XPS spectra of O-1s almost recovered after heating recovery process. However the asymmetry of XPS peak for O-1s indicates that there might be a new small XPS peak for O-1s at about 538 eV after TDS. For convenience the XPS peak for O-1s at 536.1 eV is labeled as O- $\alpha$ , that at 533.2 eV as O- $\beta$  and that at 531.3 eV as O- $\gamma$ .

The Si-2p XPS spectra of  $\text{Li}_4\text{SiO}_4$  before  $\text{D}_2^+$ -irradiation, after  $\text{D}_2^+$ -irradiation and after heating recovery process are compared in Fig. 3. The binding energy of electron (BE) for Si-2p is mainly observed at 107.1 eV before  $\text{D}_2^+$ -irradiation. And multiple XPS peaks for Si-2p are observed at the range of 95–110 eV after 3 keV  $\text{D}_2^+$ -irradiation at R.T. It is considered that the XPS spectra of Si-2p after irradiation consist of three XPS peaks, namely, the first is at 107.1 eV, the second is at 104.2 eV, and the third is at 99.7 eV. It is also observed that the XPS spectra of Si-2p almost recovered after heating recovery process. However the BE of main XPS peak for Si-2p (107.7 eV) after heating recovery process is about 0.6 eV higher than that before irradiation. For convenience the XPS peak for Si-2p at 107.1 eV is labeled as Si- $\alpha$ , that at 104.2 eV as Si- $\beta$  and that at 99.7 eV as Si- $\gamma$ .

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