

# Correlation between annihilation of irradiation defects and tritium release behavior for advanced tritium breeding material $\text{Li}_{2+x}\text{TiO}_3$

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The effect of lithium concentration on tritium release behavior for  $\text{Li}_{2+x}\text{TiO}_3$  was investigated and the correlation between annihilation of irradiation defects and tritium release was studied. To evaluate the kinetics of irradiation defect annihilation, Electron Spin Resonance (ESR) measurement was applied for neutron-irradiated  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2+x}\text{TiO}_3$  such as  $\text{Li}_{2.4}\text{TiO}_3$ . It was found that two irradiation defects, E'-centers and O-centers, were formed for those samples. The annihilation of E'-centers for  $\text{Li}_{2.0}\text{TiO}_3$  proceeded at around 600 K, although that for  $\text{Li}_{2.4}\text{TiO}_3$  were observed in the temperature range between 400 K and 700 K. In addition, tritium release, namely Peak 1 and Peak 2, were observed around 470 K and 600 K for  $\text{Li}_{2+x}\text{TiO}_3$ . A crystal structure of  $\text{Li}_{2+x}\text{TiO}_3$  was found to be a mixture of  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{TiO}_4$  crystals. Therefore, Peak 1 and Peak 2 were attributed to release of tritium retained in  $\text{Li}_4\text{TiO}_4$  and  $\text{Li}_{2.0}\text{TiO}_3$  structures, respectively. These facts indicated that irradiation defects formed in  $\text{Li}_4\text{TiO}_4$  structure was annihilated easily compared to  $\text{Li}_{2.0}\text{TiO}_3$ , leading to tritium release at lower temperature of 400 K as Peak 1 in  $\text{Li}_4\text{TiO}_4$ .

Keywords: Solid breeding material, blanket, lithium titanate, irradiation defect, ESR, TDS

## 1. Introduction

For the development of D-T fusion reactors, it is important to establish an effective fuel recycling system. In the test blanket module for ITER, lithium titanate ( $\text{Li}_2\text{TiO}_3$ ), one of ternary lithium oxides, is selected as tritium breeding materials due to good tritium release, high chemical stability, and so on [1]. Because tritium as fuel must be produced in D-T fusion reactors, one of the key roles of  $\text{Li}_2\text{TiO}_3$  is the tritium generation. For the steady state reactor operation, sufficient amount of tritium must be generated in blanket system to keep fuel cycle of the reactors. However, the concentration of lithium in  $\text{Li}_2\text{TiO}_3$  will be decreased by the consumption by the reaction of  ${}^6\text{Li}(n, \alpha)\text{T}$  and  ${}^7\text{Li}(n, n\alpha)\text{T}$  during D-T fusion reactor operation. The vaporization of lithium will also reduce the lithium concentration in  $\text{Li}_2\text{TiO}_3$ , resulting in the reduction of tritium generation rate with reactor operation. Therefore, the use of  $\text{Li}_{2.0}\text{TiO}_3$  with lithium enrichment, such as  $\text{Li}_{2.2}\text{TiO}_3$ ,  $\text{Li}_{2.4}\text{TiO}_3$  ( $\text{Li}_{2+x}\text{TiO}_3$ ) is considered to increase the tritium generation rate in  $\text{Li}_{2.0}\text{TiO}_3$ .

Tritium generated in  $\text{Li}_2\text{TiO}_3$  migrates in the grain via various processes such as trapping and de-trapping at trapping sites, diffusion in the interstitial of lattice and recombination on the surface. Understanding of tritium migration mechanisms is quite important for stable extraction of tritium from the blankets. The interaction between generated tritium and  $\text{Li}_{2.0}\text{TiO}_3$  will be changed with an increase in lithium concentration, because of the amount of generated tritium, the change of crystal structure,

stability of trapping site and so on.

Especially for understanding tritium release mechanisms, tritium release behaviors from  $\text{Li}_{2.0}\text{TiO}_3$  and lithium enriched sample ( $\text{Li}_{2+x}\text{TiO}_3$ ) were investigated by means of Thermal Desorption Spectroscopy (TDS) [2, 3] in our previous study. Tritium TDS spectrum of  $\text{Li}_{2.0}\text{TiO}_3$  consisted of single release stage at around 600 K under the constant heating rate of 0.5 K/min. The rate-determining step of tritium release was evaluated as the tritium diffusion process in  $\text{Li}_{2.0}\text{TiO}_3$  from the results of kinetic analyses. Tritium TDS spectra for  $\text{Li}_{2+x}\text{TiO}_3$  were consisted of two release stages at around 470 K and 600 K. The tritium release stage around 600 K was derived from the tritium diffusion in  $\text{Li}_{2.0}\text{TiO}_3$ . It was found that the amount of tritium released at the additional release peak (450 K) for  $\text{Li}_{2+x}\text{TiO}_3$  was increased with the increase in lithium concentration. It was expected that tritium release for  $\text{Li}_{2+x}\text{TiO}_3$  would be controlled not only by  $\text{Li}_{2.0}\text{TiO}_3$  structure but also by  $\text{Li}_4\text{TiO}_4$  structure, which was formed by the excess lithium concentration [4]. Recent tritium TDS measurements for  $\text{Li}_4\text{TiO}_4$  showed tritium release stages were located at 450 K and 600 K, suggesting that tritium release stage at lower temperature for  $\text{Li}_{2+x}\text{TiO}_3$  would be derived from the tritium release from  $\text{Li}_4\text{TiO}_4$ . These facts indicated that the tritium release mechanisms in  $\text{Li}_{2+x}\text{TiO}_3$  would be controlled by the both structures of  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_4\text{TiO}_4$ .

For the estimation of tritium inventory in  $\text{Li}_{2+x}\text{TiO}_3$ , the elucidation of tritium trapping and de-trapping

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processes in  $\text{Li}_{2+x}\text{TiO}_3$  is also important. The irradiation defects are considered to act as trapping sites for tritium in solid breeding materials, indicating that tritium inventory in  $\text{Li}_{2+x}\text{TiO}_3$  would be controlled by the density of the irradiation defects. The irradiation defects would be annihilated with tritium de-trapping, then trapped tritium would be released. Hence, the influence for the increase of lithium concentration in  $\text{Li}_2\text{TiO}_3$  on defect behavior is a critically important subject. The evaluation for the annihilation kinetics of the defects can contribute to controlling the tritium inventory in blanket systems.

Therefore, in this study, ESR experiments for thermal neutron irradiated  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$  were performed to evaluate the behavior of irradiation defects in these materials. Both of isochronal annealing and isothermal heating were applied to elucidate the annihilation kinetics for irradiation defects.

## 2. Experimental

Powders of  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$  purchased from Kaken Co. were used as samples. These samples were introduced into quartz tubes and preheated at 1173 K under He gas with the pressure of less than a few pascal for 3 hours. After heating, thermal neutron irradiation was performed at Research Reactor Institute, Kyoto University (KURRI). The thermal neutron flux was  $5.5 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ . The thermal neutron irradiation was carried out for 10 min, corresponding to the thermal neutron fluence of  $3.3 \times 10^{15} \text{ n cm}^{-2}$ . In order to clarify the annihilation behaviors and the densities of irradiation defects for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$ , the isochronal annealing experiments from R.T. to 773 K were performed with the heating step of 25 K, with the holding time for 5 minutes. The isothermal heating experiments at the temperature range of 573 - 673 K for up to 8 hours were also done to evaluate the kinetics of defect annihilation. After each isochronal and isothermal heating step, the samples were immediately cooled to liquid nitrogen temperature. Thereafter, the ESR (Bruker Biospin EMX 8/27 EPR Spectrometer) measurements were carried out at liquid nitrogen temperature to investigate the irradiation defects in samples. The amount of defects were estimated using  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  which has a unpaired electron in each molecule [5,6].

## 3. Result and discussion

Fig. 1 shows the ESR spectrum for neutron irradiated  $\text{Li}_{2.4}\text{TiO}_3$ . It was found that the asymmetric and rather complex ESR spectrum was observed for the neutron-irradiated  $\text{Li}_{2.4}\text{TiO}_3$ . It should be noted that major defects would be induced by collision with recoiled tritium and  $\alpha$ -particle generated by the nuclear reaction of  ${}^6\text{Li}(n,\alpha)\text{T}$ , as was the case in the previous studies [7]. The signal of ESR spectrum was enhanced, indicating that the irradiation defects were formed in the sample. It was found that the ESR spectrum for neutron irradiated  $\text{Li}_{2.4}\text{TiO}_3$

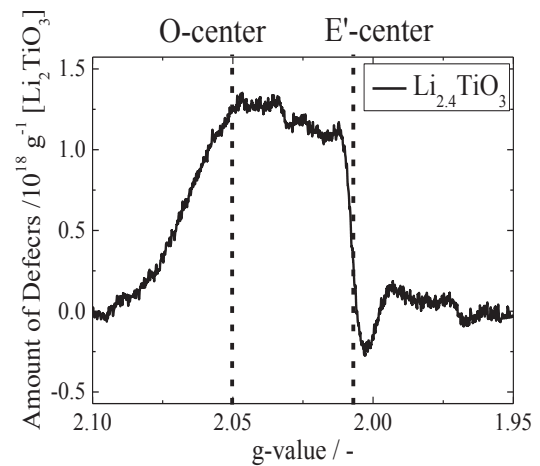


Fig.1 ESR spectrum for neutron irradiated  $\text{Li}_{2.4}\text{TiO}_3$  consisted of two kinds of irradiation defects, E'-centers and O-centers located at  $g=2.01$  and  $g=2.05$  [8-10], respectively. E'-centers are the oxygen vacancies trapping one electron and O-centers are interstitial oxygen atoms in interstitial of lattice, indicating that these irradiation defects are pair defects so called Frenkel pair. It has been considered that E'-center would act as tritium trapping sites [11]. Fig. 2 shows the annihilation behavior of E'-centers by isochronal heating for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$ , respectively. It was found that O-centers has annihilated in the same temperature region, indicating that the annihilation processes of these defects proceeded by recombination of E'-centers and O-centers. Fig. 2 clearly showed that the annihilation temperatures for E'-centers in  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$  were different and annihilation of E'-centers for  $\text{Li}_{2.0}\text{TiO}_3$  initiated above 600 K, although that for  $\text{Li}_{2.4}\text{TiO}_3$  was shifted toward lower temperature region of 400 - 700 K. Hara *et al.*, reported that  $\text{Li}_4\text{TiO}_4$  structure existed in lithium enriched samples [4]. These facts indicated that irradiation defects formed in  $\text{Li}_4\text{TiO}_4$  structure was annihilated easily compared to  $\text{Li}_{2.0}\text{TiO}_3$  resulting in the shift of annihilation temperature for  $\text{Li}_{2.4}\text{TiO}_3$ , suggesting that interstitial oxygen atoms can easily diffuse in  $\text{Li}_4\text{TiO}_4$  compared to  $\text{Li}_{2.0}\text{TiO}_3$ . Therefore, tritium trapped by irradiation defects in  $\text{Li}_4\text{TiO}_4$  can be de-trapped at lower

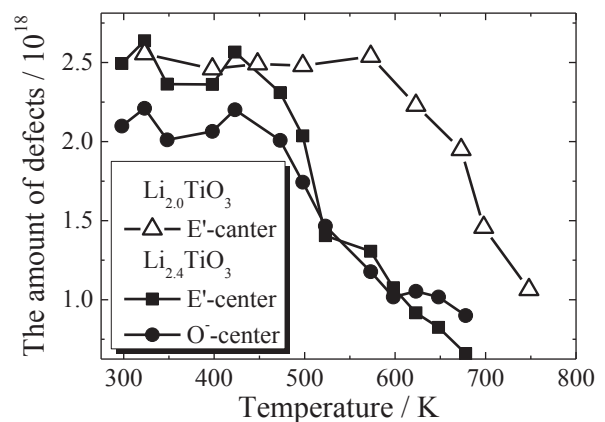


Fig.2 Annihilation behavior of E'-centers in isochronal heating for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$

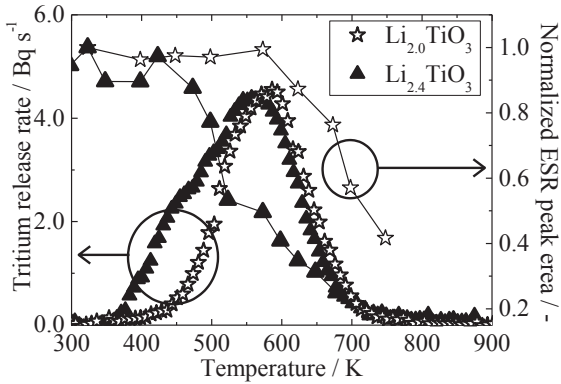


Fig.3 Comparison of TDS spectra and annihilation behaviors of E'-center

temperature than that in  $\text{Li}_{2.0}\text{TiO}_3$ .

Fig. 3 shows the comparison of TDS spectra under the heating rate of 0.5 K/min and annihilation behavior of E'-center for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$ . The TDS spectrum for  $\text{Li}_{2.4}\text{TiO}_3$  consisted of two tritium release stages. In our previous study [2], Peak 1 located at 450 K was attributed to tritium release from  $\text{Li}_4\text{TiO}_4$  structure in  $\text{Li}_{2.4}\text{TiO}_3$  and Peak 2 at around 600 K was attributed to tritium release from  $\text{Li}_{2.0}\text{TiO}_3$  structure. The tritium release temperature region for Peak 1 and the annihilation temperature region of irradiation defects formed in  $\text{Li}_{2.4}\text{TiO}_3$  were almost the same. On the other hand, the annihilation temperature region of irradiation defects formed in  $\text{Li}_{2.0}\text{TiO}_3$  was higher than 600 K, indicating that tritium in E-centers of  $\text{Li}_{2.0}\text{TiO}_3$  structure were still trapped below 600 K, indicating that tritium release as Peak 1 would be triggered by the annihilation of irradiation defects in  $\text{Li}_4\text{TiO}_4$  structure.

The typical result of the isothermal annealing experiments for  $\text{Li}_{2.4}\text{TiO}_3$  is shown in Fig. 4. The annihilation rate of E'-centers should be controlled by the first order reaction as follows,

$$N(t) = N^0 \exp(-kt) \quad (1)$$

, where  $N(t)$  is the amount of E'-center in time,  $N^0$  is the initial amount of E'-center and  $k$  is the rate constant of reaction. Kinetics of de-trapping process were defined as follows,

$$k = A \exp\left(-\frac{Ea}{RT}\right) \quad (2)$$

, where  $A$  is pre-exponential factor. The activation energy was evaluated for  $\text{Li}_{2.4}\text{TiO}_3$  by the Arrhenius type plots as shown in Fig. 5. The activation energy of annihilation for E'-center in  $\text{Li}_2\text{TiO}_3$  was evaluated about 0.5 eV [7]. Therefore the activation energies for the annihilation of E'-centers were about 0.5 eV and were almost the same for the two samples, although the annihilation temperature of E'-centers in  $\text{Li}_{2.4}\text{TiO}_3$  was lower than that in  $\text{Li}_{2.0}\text{TiO}_3$ . Two possibilities which can explain the same activation energy for the annihilation of E'-centers in  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$ , are considered. The first is due to the same

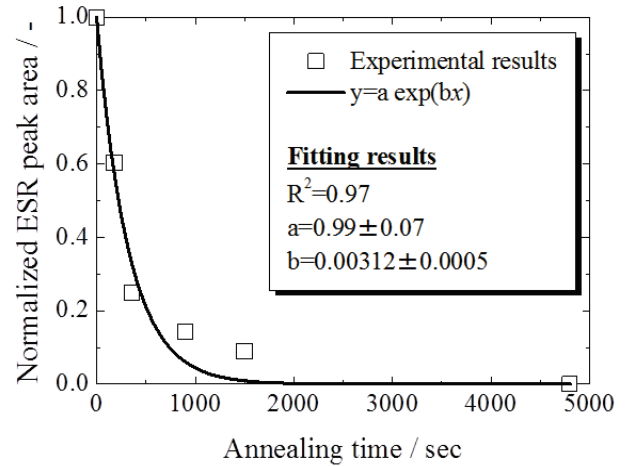


Fig.4 Typical result of isothermal experiment for  $\text{Li}_{2.4}\text{TiO}_3$

elementary process in the annihilation of E'-center. The annihilation of E'-centers takes place by the oxygen diffusion in these structures. The oxygen diffuses in the crystal structure with interacting to the constituent atoms. The  $\text{Li}_4\text{TiO}_4$  and the  $\text{Li}_{2.0}\text{TiO}_3$  structures have the same constituent atoms although the chemical bonds among these atoms are different. Therefore oxygen diffusivity may not be different substantially. The second reason is the ratio of each structure. It can be considered simply that  $\text{Li}_{2.4}\text{TiO}_3$  consists of  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_4\text{TiO}_4$  with the fraction of 80% and 20%, respectively. It can be said that the  $\text{Li}_{2.0}\text{TiO}_3$  is the predominant structure and the contribution of  $\text{Li}_4\text{TiO}_4$  structure to the apparent activation energy for the annihilation of E'-centers will be small. Consequently, the activation energy for the annihilation of E'-centers in  $\text{Li}_{2.4}\text{TiO}_3$  was similar to that in  $\text{Li}_{2.0}\text{TiO}_3$ .

The annihilation behavior of irradiation defects in  $\text{Li}_{2.4}\text{TiO}_3$  was evaluated. It was found that the irradiation defects were annihilated at lower temperature region for  $\text{Li}_{2.4}\text{TiO}_3$  compared to those in  $\text{Li}_{2.0}\text{TiO}_3$ , although the activation energy for defect annihilation was almost the same. The defect annihilation at lower temperature indicates that tritium recovery can be achieved effectively at lower temperature. Actually, the tritium release peak was observed at lower temperature region for  $\text{Li}_{2.4}\text{TiO}_3$ . In

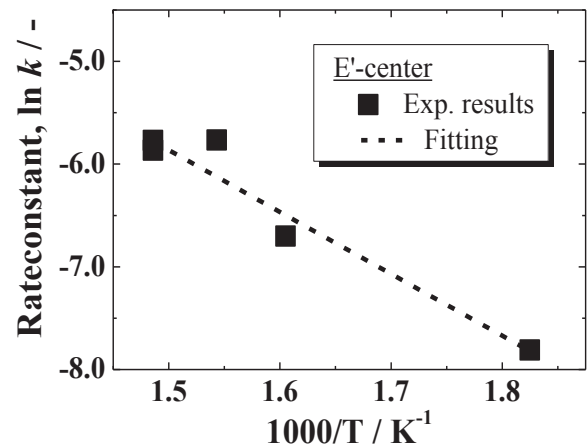


Fig.5 Analytical result for E'-center in  $\text{Li}_{2.4}\text{TiO}_3$

addition, the same activation energy of defect annihilation for  $\text{Li}_{2.4}\text{TiO}_3$  and  $\text{Li}_{2.0}\text{TiO}_3$  indicates that the increased lithium concentration would not impact the density and the stability of defects. These facts indicate that large advantage of using  $\text{Li}_{2+x}\text{TiO}_3$  in blanket system of D-T fusion reactor is expected due to easy tritium recovery and tritium inventory reduction in  $\text{Li}_{2+x}\text{TiO}_3$  compared to those in  $\text{Li}_{2.0}\text{TiO}_3$ .

#### 4. Conclusion

The effect of lithium concentration on tritium release behavior was investigated with comparison of irradiation defects and tritium release behavior. The effect of irradiation defects on tritium release behavior for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$  were studied by means of ESR. From isochronal heating experiments, the amount of  $E'$ -centers in  $\text{Li}_{2.0}\text{TiO}_3$  changed slightly in the temperature region below 600 K and its annihilation started above 600 K. However,  $E'$ -center formed in  $\text{Li}_{2.4}\text{TiO}_3$  were annihilated around 400 K to 700 K. Because  $\text{Li}_4\text{TiO}_4$  structure existed in  $\text{Li}_{2+x}\text{TiO}_3$ , the  $E'$ -centers annihilated at lower temperature in  $\text{Li}_{2.4}\text{TiO}_3$  were formed in other structure, such as  $\text{Li}_4\text{TiO}_4$ . In addition, the tritium release temperature region for Peak 1 and the annihilation temperature region of irradiation defects formed in  $\text{Li}_{2.4}\text{TiO}_3$  were almost the same. These facts indicated that tritium release as Peak 1 would be triggered by the annihilation of irradiation defects in  $\text{Li}_4\text{TiO}_4$  structure. The elucidation of tritium release kinetics was carried out by means of isothermal annihilation experiments for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_4$  to reveal the dynamics of defect annihilation for controlling tritium inventory in blanket systems. From the values of the rate constants in various heating temperatures, the activation energies were evaluated for  $\text{Li}_{2.0}\text{TiO}_3$  and  $\text{Li}_{2.4}\text{TiO}_3$  to be commonly 0.5 eV. It was explained that  $\text{Li}_{2.4}\text{TiO}_3$  consisted of large amount of  $\text{Li}_{2.0}\text{TiO}_3$  structure, and annihilation process of irradiation defects in  $\text{Li}_{2.4}\text{TiO}_3$  was controlled by annihilation rate of irradiation defects formed in  $\text{Li}_{2.0}\text{TiO}_3$ . Although the amount of defects was not increased, that of tritium released at lower temperature was increased with the increase in lithium concentration. Therefore, it was indicated that tritium inventory in  $\text{Li}_{2+x}\text{TiO}_3$  will be decreased compared to  $\text{Li}_{2.0}\text{TiO}_3$  in fusion reactors.

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