

# Correlation between Tritium Release and Thermal Annihilation of Irradiation Damages in Neutron-irradiated Ceramics Breeders

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## 1. Introduction

The high energy chemistry [1-3] is defined as the interaction of high energy particles with matter, the nature and reactivity of short-lived species induced by the action of particle and electromagnetic radiation or hot atoms on substances in their gaseous and condensed states, and chemical processes initiated in organic and inorganic systems by high energy radiation.

The high energy chemistry began from "Hot atom chemistry" which have been used as informal synonym for "recoil chemistry" or "chemical effects of nuclear transformations".

From the beginning, a hot atom means an atom formed with energy well in excess of ambient thermal energy or highly charged via a nuclear event. Recently, it has been available to study on the hot atom reaction that the hot atom can be formed by the non-nuclear reaction as well as by the nuclear event. The hot atom chemistry have become to include not only the chemistry induced via the nuclear event but also via non-nuclear reactions using beam method and/or photolysis, with the energy scale in the range from several tens to hundreds eV as shown in Fig. 1, thus it is called as the "High energy chemistry".

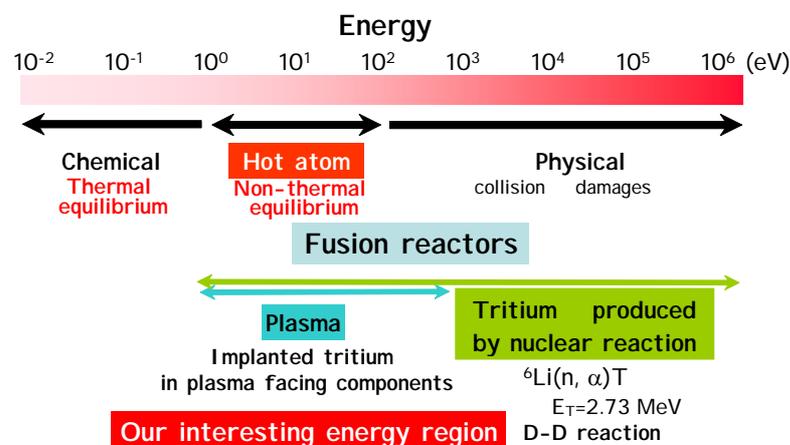


Fig. 1 Energy of tritium in fusion reactor conditions.

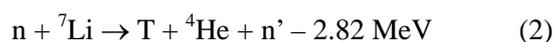
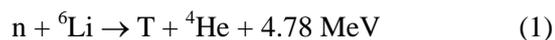
The high energy chemistry deals with chemical events caused by the deposition in single atoms of energy, which is much greater than chemical bond and ionization energies. Therefore the high energy chemical reaction progresses without any other energies such as activation energy in thermal chemical reactions. The type of energy conveyed to the atom, and thence to the surrounding atoms and molecules are: (1) the kinetic energy of recoil from gamma ray or energetic particle emissions (for example, typically of the order of 100 eV from the (n,  $\gamma$ ) process and 100,000 eV from the (n, p) process), (2) the energy of Coulomb repulsion generated when the high positive charge acquired by an atom as a result of internal conversion of  $\gamma$  rays, excitation and/or emission of inner shell electron by X-ray absorption, followed by Auger electron emission, spreads over the atom in a molecules and (3) the energy of ionization and molecular excitation conveyed to molecule of the medium by  $\gamma$  rays, X rays and high energy electrons emitted. The recoil energy and massive Coulomb repulsion are different initiators of reactions than those found in radiation chemistry, but the reactions of electrons, atoms, radicals, and ions following the primary energy deposition are similar.

### 1.1 Application of high energy chemistry to fusion reactor research

In fusion reactors, there is possibility that high energy chemistry of tritium would play important roles in breeder materials and plasma facing components, as shown in Fig. 1.

In the blanket, the recoil tritium is produced by the  ${}^6\text{Li}$  (n,  $\alpha$ ) T and  ${}^7\text{Li}$  (n, n' $\alpha$ ) T reactions. Its final states would be independent of primary species, and classical thermodynamics and

kinetics of thermal species will govern the behavior of the tritium, although the chemical effects of nuclear transformation obviously enter the scene in the very first stage of exposure to neutron. Energetic tritium can be produced with the neutron capture reactions of lithium as follows.



It is important to investigate that what kind of tritium chemical form is induced by high energy chemical reaction during neutron irradiation because these information should be considered in the tritium recovery concepts from the blanket.

In the present study, high energy chemistry of tritium produced in tritium solid-breeder materials will be present mainly focused on our experimental results for  $\text{Li}_2\text{O}$ .

## 2. High energy chemical issues in solid breeding materials

### 2.1 Experimental method

#### 1) Neutron irradiation

The degassed materials ( 10-20 mg ) were sealed in quartz ampoules under vacuum and irradiated in the T- pipe of the JRR-4 reactor of the Japan Atomic Energy Research Institute. The thermal and fast neutron fluxes at the irradiation position, monitored with Co and Ni foils, were  $4 \times 10^{13}$  and  $3 \times 10^{12} \text{ cm}^{-2}\text{s}^{-1}$ , respectively. The temperature at the target surface was about 320 K . The irradiated materials were stored in a container cooled with liquid nitrogen.

## 2) Analytical procedures

The tritium species ( $T^+$ ,  $T^-$  and  $T^0$ ) existing in  $Li_2O$ ,  $LiOH$  and  $LiH$  crystals were analyzed with a radiometric method based on the following reactions [4]. When the irradiated material is dissolved in heavy water, the labile tritium ( $T^+$ ) in the solid is converted to tritiated water through the immediated exchange reaction,



or



Tritide anion ( $T^-$ ), which would be bonded to  $Li^+$ , gives rise to gaseous DT on hydrolysis,



The exchange between tritium ( $T^0$ ), which would be in the form of molecular hydrogen ( $HT$ ,  $T_2$ ) as well as hydrocarbons, and deuterium of heavy water is very slow in absence of catalysts, so that the  $T^0$  species is evolved in tile form of  $HT$ ,  $T_2$  and hydrocarbon-T. Consequently the tritium remaining in the aqueous phase corresponds to the  $T^+$  species. The  $T^-$  species is observed as gaseous DT and can be separated from the  $T^0$  species which is evolved as  $HT$ ,  $T_2$  and hydrocarbon-T.

Details of the apparatus and the analytical

procedures were described in the previous paper [5].

### 2.2 Tritium existing states [5-9]

In neutron-irradiated  $Li_2O$  crystals, tritium was found to exist in the  $T^+$ ,  $T^-$  and  $T^0$  states. The abundance of these species is listed in Table 1, together with other data to be compared. The value is an "initial" abundance obtained for the material which was not subjected to any heat treatment after the neutron irradiation.

Although the most abundant species was  $T^+$  in the  $Li_2O$  crystals irradiated with neutrons, it is to be noticed that the initial abundance of  $T^+$  was obviously low compared with the value obtained for unirradiated  $Li_2O$  crystals in which tritium was thermally doped at 470 K under equilibrium with gaseous HT. In the latter case more than 99.99% of tritium was found in the  $T^+$  state. Also in neutron-irradiated  $LiOH$  crystals, nearly 100% of tritium was in the  $T^+$  state as listed in Table 1. On the contrary, almost all of the tritium was found in the  $T^-$  state in  $LiH$  crystals irradiated with neutrons. The  $T^+$  species in  $LiOH$  crystals is considered to be in the form of  $OT$ , while the  $T^-$  state of tritium in  $LiH$  crystals would be bound to  $Li^+$  ions. The presence of  $T^-$  in neutron-irradiated  $Li_2O$  crystals suggests that there should be positive sites which have strong affinity for  $T^-$  ions in the crystal.

Table 1 Tritium species existing in lithium oxide crystals irradiated with neutrons.

Material	Neutron fluence (cm <sup>-2</sup> )	Initial abundance (%)				
		T <sup>+</sup>	T <sup>-</sup>	T <sup>0</sup>		
				HT	T <sub>2</sub>	Hydrocarbons
Li <sub>2</sub> O	2.5 × 10 <sup>15</sup>	75.8 ± 2.8	22.2 ± 2.7	1.7 ± 0.5	0.2 ± 0.3	0.1 ± 0.05
	2.5 × 10 <sup>16</sup>	66.9 ± 1.6	31.0 ± 1.0	1.5 ± 0.5	0.3 ± 0.05	0.5 ± 0.1
	8.3 × 10 <sup>17</sup>	77.2 ± 2.6	22.0 ± 2.7	0.1 ± 0.01	0.3 ± 0.04	0.4 ± 0.2
LiOH	2.5 × 10 <sup>16</sup>	99.97 ± 0.01	0.01 ± 0.01	0.02 ± 0.01	n.d.	n.d.
LiH	2.5 × 10 <sup>16</sup>	1.3 ± 0.1	97.8 ± 0.5	0.9 ± 0.1	n.d.	n.d.
Li <sub>2</sub> O	Unirradiated <sup>a</sup>	99.93 ± 0.01	n.d.	0.07 ± 0.06	n.d.	n.d.
LiOH	Unirradiated <sup>a</sup>	99.99 ± 0.01	n.d.	0.007 ± 0.005	n.d.	n.d.

<sup>a</sup> The tritium was thermally doped. n.d.: Not detected.

To understand the nature of  $T^+$  and  $T^-$  species in  $Li_2O$  crystals irradiated with neutrons, thermal behavior of the tritium species was investigated. Fig. 2 illustrates the relative abundance of  $T^+$ ,  $T^-$  and  $T^0$  species in  $Li_2O$  crystals as a function of the heating temperature. The sample was heated at prescribed temperatures for 10 min, without breaking the quartz ampoule used for the neutron irradiation. A distinct temperature dependence was observed in the abundance of all but  $T^0$  species. The  $T^+$  fraction in the crystals irradiated to  $2.5 \times 10^{15}$  and  $2.5 \times 10^{16} \text{ cm}^{-2}$  increased to 93% or more when the crystal was heated at 570 K. Quite a reverse feature was true for the  $T^-$  species and its abundance became only 5% at 570 K. The same trend was observed for the crystals irradiated to  $8.3 \times 10^{17} \text{ cm}^{-2}$  although the curves shifted to somewhat higher temperature. In the present experiment, the upper temperature of isochronal heating was limited to 570 K because the considerable amount of tritium was released from the crystal at higher temperatures. Anyway it was the experimental evidence that  $T^+$  was the most stable state in  $Li_2O$  crystals. Alternatively, radiation damages induced by the neutron irradiation would possibly contribute to the existence of the  $T^-$  state of tritium. It is interesting to note that the difference between the initial and maximum abundance of  $T^-$ ,  $\Delta A = A_{\text{max}} - A_{\text{init}}$ , became larger with increasing neutron fluence, although no distinct neutron fluence dependency was observed in the initial abundance of  $T^-$ . High energy tritons (2.7 MeV) and helium ions (2.1 MeV) can contribute to the production of radiation damage in  $Li_2O$  crystals. The typical radiation damage induced by the  ${}^6\text{Li}(n, \alpha)T$  reaction in  $Li_2O$  has been reported to be  $F^+$  centers (oxygen-ion vacancy

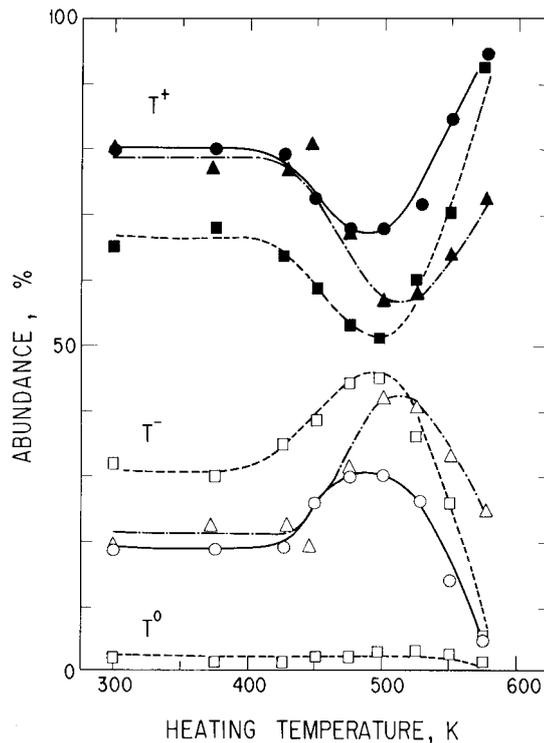


Fig. 2 Abundance of  $T^+$ ,  $T^-$  and  $T^0$  species in  $Li_2O$  as a function of the heating temperature. The samples were heated for 10 min at each temperature after neutron irradiation to  $2.5 \times 10^{15}$  ( , ),  $2.5 \times 10^{16}$  ( , ) and  $8.3 \times 10^{17} \text{ cm}^{-2}$  ( , ).

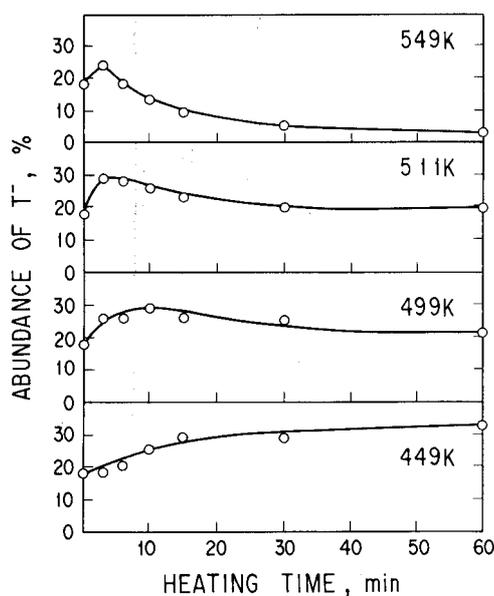


Fig. 3 Isothermal change of  $T^-$  abundance in  $Li_2O$  irradiated with neutrons.

occupied by one electron) [10]. The  $F^+$  center can act as a positive site where tritium is trapped in the  $T^-$  state.

Fig. 3 illustrates the  $T^-$  abundance in the  $Li_2O$  crystal irradiated to  $2.5 \times 10^{15} \text{ cm}^{-2}$  as a function of the isothermal heating time. In  $Li_2O$  crystals heated below 500 K, the  $T^-$  abundance increased monotonically, while the  $T^-$  abundance in the crystal heated above approximately 500 K showed a maximum. Appearance of the maximum in these curves suggests the presence of two competitive reactions; the  $T^+$ -to- $T^-$  conversion and its inverse. Although reaction rates of both the conversions became higher with increasing temperature, the rate of the  $T^-$ -to- $T^+$  conversion was enhanced above 500 K and the maximum appeared the earlier, the higher the temperature. The  $T^+$ -to- $T^-$  conversion, which took place in preference to the  $T^-$ -to- $T^+$  conversion, might be attributed to the interaction of tritium with  $F^+$  centers.

On the other hand, the  $T^-$ -to- $T^+$  conversion observed above 500 K can be explained in terms

of the recovery of  $F^+$  centers through thermal annealing. The presence of  $T^+$  species would become less probable with decreasing concentration of  $F^+$  centers. In fact, Noda et al. [10] have reported from their ESR measurements that the  $F^+$  center produced in  $Li_2O$  is annihilated by heating above 400 K. In Fig. 4, their experimental result is superimposed on the change in the abundance of  $T^+$  and  $T^-$  species obtained for the  $Li_2O$  crystals irradiated to approximately the same neutron fluence ( $3.8 \times 10^{16} \text{ cm}^{-2}$  for the former and  $2.5 \times 10^{16} \text{ cm}^{-2}$  for the latter). The  $T^-$ -to- $T^+$  conversion above 500 K seems to be closely correlated to the annihilation of  $F^+$  centers in  $Li_2O$  crystals. The increase of the  $T^-$  fraction in the temperature range between 400 and 500 K of the isochronal heating for 10 min (Figs. 2 and 4) reflected the preferential  $T^+$ -to- $T^-$  conversion as observed at early time of the isothermal heating (Fig. 3).

In conclusion, the presence of the  $T^-$  species in  $Li_2O$  crystals irradiated with neutrons is ascribed to the interaction of tritium with  $F^+$  centers. The  $T^-$  species has a nature to be converted to the stable  $T^+$  species through heat treatments above 500 K. In relation to the thermal release of tritium from neutron-irradiated  $Li_2O$  above 570 K, it is possible to conclude that the tritium diffuses in the  $T^+$  form, which would be bound to  $O^{2-}$  ions in the crystal. Fig. 4 also suggests that tritium behavior in  $Li_2O$  crystal could be correlated with annihilation of the irradiation damages. In our recent studies, the similar correlation has observed for other lithium oxides [11-14].

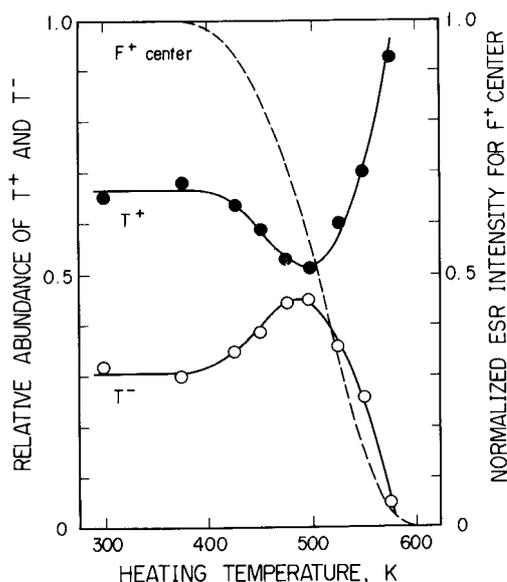
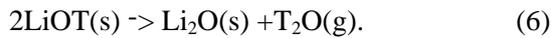


Fig. 4 Comparison of the change in  $T^+$  and  $T^-$  abundances in  $Li_2O$  with the feature of  $F^+$  center annihilation.

### 3. Energetic Tritium release mechanism [15-20]

The fundamental tritium release behavior of neutron-irradiated  $\text{Li}_2\text{O}$  crystals can be interpreted in the following mechanism (Fig. 5), which consists of two major processes: the  $\text{T}^+$  diffusion in the crystal and the evolution of  $\text{T}_2\text{O}$  molecules as a result of the reaction



Tritium produced by the  ${}^6\text{Li}(\text{n}, \alpha)\text{T}$  reaction has 2.73 MeV of initial kinetic energy associated with the nuclear recoil event. This high-energy triton loses its kinetic energy penetrating through  $\text{Li}_2\text{O}$  crystals as far as  $30.8 \pm 2.5 \mu\text{m}$ . The tritium is thermalized in the crystal sharing three different valences ( $\text{T}^+$ ,  $\text{T}^-$  and  $\text{T}^0$ ), although distribution of the valence states depends upon the irradiation conditions. The most abundant species in  $\text{Li}_2\text{O}$  crystal is  $\text{T}^+$ , and its fraction increases with increasing neutron fluence. Internal heat and radiation damage induced by the neutron irradiation would play a role in determining the abundance of  $\text{T}^+$  species.

If the neutron-irradiated  $\text{Li}_2\text{O}$  crystals are heated under vacuum, the  $\text{T}_2\text{O}(\text{g})$  release becomes apparent around 500 K. The origin of the  $\text{T}_2\text{O}$  molecule is the  $\text{T}^+$  species which might be in the form of  $\text{OT}^-$  or  $\text{LiOT}$  in the vicinity of the solid surface. The  $\text{T}_2\text{O}$  molecule is evolved via reaction (6).

At temperatures above 500 K, the tritium species other than  $\text{T}^+$  existing in the crystal are converted into the  $\text{T}^+$  species and begin to migrate outward, interacting with  $\text{O}^{2-}$  the matrix. The diffused  $\text{T}^+$  species forms  $\text{LiOT}$  at the surface and is also released via reaction (6). At

temperatures below 570 K, however, the rate of reaction (6) to the right is still lower than that of the  $\text{T}^+$  diffusion, and the overall tritium release rate is controlled by the thermal decomposition of  $\text{LiOT}$  at the surface.

At higher temperatures ( $>570 \text{ K}$ ), the thermal decomposition of  $\text{LiOT}$  proceeds much faster than the bulk diffusion of  $\text{T}^+$ , so that the  $\text{HTO}$  molecules are evolved as soon as  $\text{T}^+$  reaches the surface. Consequently, the bulk diffusion of  $\text{T}^+$  becomes the rate-determining step of the  $\text{T}_2\text{O}(\text{g})$  release process above 570 K. At this time, however, it is to be noted that the reversible reaction of eq. (6) is controlled by the partial pressure of  $\text{T}_2\text{O}(\text{g})$  or  $\text{H}_2\text{O}(\text{g})$  over the solid. The immediate evolution of  $\text{T}_2\text{O}$  molecules would occur under the condition where the partial pressure of the water species is maintained below the equilibrium pressure.

In addition to the above mentioned major processes through which most of the tritium produced in  $\text{Li}_2\text{O}$  crystals is released in the chemical form of  $\text{T}_2\text{O}$ , there are minor processes leading to the  $\text{T}_2$  evolution. A fraction of the  $\text{T}$ -species which might be bonded to  $\text{Li}^+$  is released via the reaction analogous to  $\text{LiH}(\text{s}) \rightarrow \text{Li}(\text{s}, \text{l}) + 1/2\text{H}_2(\text{g})$ . The  $\text{T}^0$  species which might be present as molecular tritium in solid is also a source of  $\text{T}_2$ .

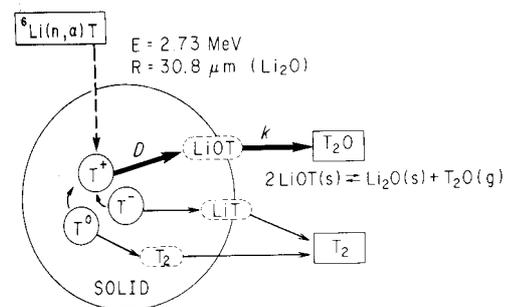


Fig. 5 Tritium release mechanism from  $\text{Li}_2\text{O}$ .

The mechanism presented here could be applicable to explain the fundamental behavior of tritium release not only from Li<sub>2</sub>O crystals but also from other lithium oxides.

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