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Annihilation behavior of irradiation defects in Li_4SiO_4 irradiated with high thermal neutron fluence

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ABSTRACT

The annihilation behavior of irradiation defects in Li_4SiO_4 which were irradiated with thermal neutrons to a high fluence was studied by electron spin resonance (ESR). It was observed that the ratio of O-related centers to E'-centers increased with increasing annealing temperature. The total irradiation defects were annihilated through two processes, namely the fast (120–250 °C, 70%) and the slow ones (250–500 °C, 30%), and their activation energies were determined to be 0.63 ± 0.09 and 0.89 ± 0.14 eV, respectively. The observed annihilation behavior of irradiation defects in Li_4SiO_4 was found to be very different from that in a previous study, which could be attributed to the difference in concentration and types of irradiation defects generated by different neutron fluences. It was implied that the annihilation behavior of irradiation defects in ternary lithium oxides would become more complicated with increasing neutron fluence.

1. Introduction

Lithium based ceramics, such as Li_4SiO_4 and Li_2TiO_3, are widely studied as promising tritium breeder materials for solid-type blankets of fusion reactors [1]. In China, Li_4SiO_4 has been selected as the reference tritium breeder material for the CN HCCB-TBM to be tested in ITER [2]. During the operation of fusion reactors, ceramic breeder materials will be attacked by energetic neutrons with energies up to 14 MeV, recoil tritium (2.7 MeV) and helium ions (2.1 MeV) produced by $^6Li(n, \alpha)T$ reactions. Accordingly, generation of various irradiation defects (e.g. lithium/oxygen vacancies) in the ceramic breeder materials are expected. For the design of breeding blanket systems, the effect of irradiation defects on tritium release process in ceramic breeder materials is of special concern [3]. In fact, a lot of experimental studies have shown that irradiation defects can act as tritium trapping sites and influence significantly tritium release temperature and chemical form of released tritium [3–13]. From the perspective of developing a tritium release model, it is important to understand the production and annihilation behavior of irradiation defects in ceramic breeder materials [14–16]. Particularly, Okuno et al. have suggested that there is a correlation between the annihilation process of irradiation defects and tritium release process [4,12]. In this study, we mainly focused on the annihilation process of irradiation defects in neutron-irradiated Li_4SiO_4.

2. Literature review

Since the early 1980s, some researchers (mainly from Japan) have shown interest in the annihilation behavior of irradiation defects in ceramic breeder materials due to its importance for understanding the tritium release behavior. In previous studies, isochronal and isothermal annealing experiments were performed on candidate breeder materials such as Li_2O, Li_4SiO_4, Li_2TiO_3, $LiAlO_2$, Li_2ZrO_3 and Li_2SiO_3 which were irradiated by neutrons or other methods, and electron spin resonance (ESR) method was applied to analyze the annihilation process of irradiation defects. Although extensive studies were devoted to elucidating the annihilation process of irradiation defects, relatively little research has been centered on the influence of irradiation condition on the annihilation behavior of irradiation defects.

Annihilation behavior of F^+-centers, which is an oxygen vacancy

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trapping an electron, and colloidal lithium generated in Li_2O by thermal neutrons was studied by Noda et al. [17,18]. It was found that the concentration of F^+-centers decreased in the temperature range of 147–357 °C, and the annihilation temperature of F^+-centers increased with increasing neutron fluence. The difference of the annihilation temperature of F^+-centers in neutron fluence was suggested to be attributed to the difference in the amount and distribution of F^+-centers. On the other hand, the colloidal centers increased in the temperature range of 147–327 °C and decreased with temperatures above 327 °C, to disappear above 597 °C. Vajda and Beuneu studied the production and annihilation behavior of colloidal species in Li_2O which were irradiated with 1-MeV electrons at the temperature range of −252–2 °C [19]. However, they have observed a different temperature dependence of the production and annihilation process of colloidal species from that of Noda et al. [17]. Kobayashi et al. studied the annihilation behavior of gamma-ray induced defects in Li_2O and suggested that some of F^+-centers were aggregated in the temperature range between 77 and 127 °C and decomposed above 227 °C [20]. The above studies have shown that the annihilation behaviors of F^+-centers and colloidal lithium in Li_2O were strongly dependent on irradiation conditions.

Since 2000s, a series of studies on the annihilation behavior of irradiation defects in ternary lithium oxides were also carried out. Akahori et al. studied the annihilation behavior of irradiation defects and its correlation with tritium release behavior in thermal neutron-irradiated Li_4SiO_4 [21]. After that, similar studies on Li_2TiO_3, $LiAlO_2$ and Li_2ZrO_3 were conducted by Oyaidzu et al. [22–25]. In addition, a comparison study between Li_2SiO_3 and Li_4SiO_4 was conducted by Nishikawa et al. [26]. All the above studies have shown that the annihilation of irradiation defects in neutron-irradiated ternary lithium oxides consisted of two processes, namely the fast and the slow ones. The annihilation processes of irradiation defects were analyzed by a first-order reaction model and the activation energies for the fast and the slow processes were determined accordingly. Based on the activation energies, the fast annihilation process was attributed to diffusion of trapped electrons into the defects mainly, whereas the slow annihilation process was attributed to annihilation of F^+- or E'-centers (congeneric with the F^+-centers) by recovering oxygen ions (O^-) to their own sites [26,27]. It was also suggested that the kinetics of the annihilation processes of F^+- or E'-centers was dominated by the population of oxygen vacancy under thermal equilibrium [27]. However, it should be noted that all the above results were obtained under the condition of low neutron fluence (3.3×10^{15} or 1.0×10^{16} n cm^{-2}).

A comparison study between the annihilation behaviors of irradiation defects in Li_4SiO_4 which were irradiated by 14 MeV and thermal neutrons, respectively, was carried out by Ishikawa et al. [28]. It was found that the activation energy for the slow annihilation process of irradiation defects in the 14 MeV neutron-irradiated Li_4SiO_4 was much smaller than that in the thermal neutron-irradiated one. This result was attributed to the influence of the difference in the densities of irradiation defects generated by thermal and 14 MeV neutrons [28]. Further studies were dedicated to elucidating the annihilation behavior of gamma-ray induced defects in Li_2TiO_3. Suzuki et al. reported that the annihilation temperature of E''- and O^--centers, which are Frenkel pair, in the gamma-ray irradiated Li_2TiO_3 (277–377 °C) was higher than that in the neutron-irradiated one (127–227 °C) [29]. Osuo et al. reported that the activation energy for the annihilation process of gamma-ray induced defects in Li_2TiO_3 increased with increasing gamma-ray dose [30]. It was suggested that the annihilation process of gamma-ray induced defects in Li_2TiO_3 was dominated by pyrolysis of O_2^--center [30]. The above studies indicated that further efforts are necessary to have a better understanding of the annihilation behavior of irradiation defects in ternary lithium oxides under different irradiation conditions. This study was aimed at gaining insight into the annihilation behavior of irradiation defects in Li_4SiO_4 ceramic pebbles which were irradiated by thermal neutrons to a high fluence (4.0×10^{18} n cm^{-2}).

3. Experimental

The experimental samples used in this study are Li_4SiO_4 ceramic pebbles which were fabricated by a wet method [31]. The main characteristics of the Li_4SiO_4 ceramic pebbles are shown in Table 1. Before neutron irradiation, the samples were heated at 850 °C for 2 h under helium atmosphere to remove the surface adsorbed water and other impurities (e.g. lithium hydroxide and lithium carbonate). Then the samples were sealed in quartz capsules filled with 90 kPa helium gas. Neutron irradiation of the quartz-encapsulated samples was carried out at the China Mianyang Research Reactor (CMRR) in the Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics. The samples were exposed to a thermal neutron flux of 1.57×10^{13} n $cm^{-2}s^{-1}$ for 72.5 h, and the total neutron fluence was approximately 4.0×10^{18} n cm^{-2}. The temperature of the samples during neutron irradiation was estimated to be lower than 100 °C by a numerical simulation method.

Irradiation defects generated in the neutron-irradiated samples were analyzed by ESR (BRUKER ELEXSYS E500). For ESR measurement, the samples after irradiation were transferred to a quartz tube and sealed in air immediately. Both isochronal and isothermal annealing experiments were performed to study the annihilation behavior of irradiation defects. In the isochronal annealing experiments, the annealing temperature was increased stepwise from room temperature (RT) up to the temperature where the ESR signals became too small to be detected. The temperature interval between two annealing steps was 25 °C, and the duration time of each annealing step was 5 min. After each annealing step, the sample was immediately cooled to liquid nitrogen temperature, and the ESR measurement was carried out at RT subsequently. Isothermal annealing experiments were performed to study the annihilation kinetics of irradiation defects. The isothermal annealing temperatures were selected at 250, 300, 350 and 400 °C according to the isochronal annealing experiments. Each isothermal annealing experiment was carried out until the ESR signals became too small to be detected or showed little further change. All the measurements were carried out in the same manner as that in the isochronal annealing experiments.

4. Results and discussion

Fig. 1 shows the ESR spectra of neutron-irradiated and non-irradiated Li_4SiO_4 samples. The characteristics of the ESR spectra indicated that three kinds of fundamental defects namely the so-

Table 1
Main characteristics of the Li_4SiO_4 ceramic pebbles.

Pebble diameter (mm)	Li-6 enrichment (%)	Density (%TD)	Grain size (μm)	Phase purity (%)	Crush load (N)
1.0 (av)	7.5	~80	10–50	>95	20 (av)

av: average.