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Mechanism of vacuum-annealing defects and its effect on release behavior of hydrogen isotopes in Li_2TiO_3

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ABSTRACT

Li_2TiO_3 is one of the most promising candidates among solid breeder materials. However, defects introduced into Li_2TiO_3 will act as the strong trapping sites for tritium. In the present study, mechanism of vacuum-annealing defects and its effect on release behavior of hydrogen isotopes in Li_2TiO_3 were investigated by means of X-ray diffraction, Raman spectroscopy, electron spin resonance and thermal desorption spectroscopy. The color of samples becomes dark blue and the defects were found to be introduced into Li_2TiO_3 when annealed in vacuum. This color change suggests the change from Ti^{4+} to Ti^{3+} due to decrease in oxygen content. The color recovers to white again after annealing in air. X-ray diffraction and Raman spectroscopy results indicate that there are no modifications on Li_2TiO_3 crystal phases, but on crystallinity. The main vacuum-annealing defects are E-centers and no other obvious types of defects were observed from electron spin resonance. Based on the experimental results, the production of defects by annealing in vacuum should be satisfied to the following conditions: (1) Li_2TiO_3 has been exposed in air more than 1 day; (2) Li_2TiO_3 must be annealed at the temperature higher than 300 °C; (3) Li_2TiO_3 should be annealed in vacuum lower than 10 Pa. E-centers formed under vacuum-annealing processes have considerable effects on release behavior of hydrogen isotopes investigated by thermal desorption spectroscopy and further should be considered in future fusion reactor. The present work gives some suggestions for future fusion reactors: (1) Li_2TiO_3 should be preserved in vacuum or kept from water vapor; (2) Li_2TiO_3 should be annealed at high temperature to remove the adsorbed water before loading into the facility, and must be finished within two days to avoid defects coming from reduction; (3) Li_2TiO_3 should be improved by adding more oxygen or other elements to refrain from defects introduced by reduction reaction.

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Introduction

In the future deuterium-tritium (D-T) fusion reactors, solid breeder blanket has two roles, namely, to breed tritium and to convert the energy of neutrons into heat [1,2]. In the operation of D-T fusion reactors, tritium will be offered by the reactions of ^{6}Li (n, α) T and ^{7}Li (n, nα) T in solid tritium breeding materials. Lithium titanate (Li_2TiO_3), one of ternary lithium oxides, will be selected as one of the candidates due to its good tritium release, high chemical stability, low tritium inventory, and so on [3–5].

For future fusion reactor, Li_2TiO_3 was inevitable to expose in air when loaded into fusion facility. The thermal performance of Li_2TiO_3 after exposing in air should be investigated. The color of Li_2TiO_3 which has been exposed in air changed from white to dark blue after annealing in vacuum. Moreover, E-centers, which are oxygen vacancies occupied by one electron, were introduced into Li_2TiO_3 investigated by electron spin resonance (ESR). Many researchers have reported that E-centers are considered to be promising defects for trapping tritium and trigger the detrapping and release of tritium [6–10]. The defects produced by annealing in vacuum were called 'vacuum-annealing defects' in this paper. However, there is no report on the thermal performance of Li_2TiO_3 after exposing in air and no report on the influence of this change on the performance of the tritium breeding blanket.

Previous studies [11] reported that mass of the Li_2TiO_3 samples was found to decrease with time in a hydrogen atmosphere, then to increase after the change of the atmosphere from hydrogen to oxygen. These results suggest oxygen deficient defects in Li_2TiO_3. The color of the samples was observed to change from white to dark blue under a hydrogen atmosphere. Based on the report [12], Li_2TiO_3 samples will be reacted with reducing gas. The color change suggests the change from Ti^{4+} to Ti^{3+} due to decrease in the oxygen content. This work focuses on the basic formation mechanism of vacuum-annealing defects, as well as the influence of these defects on release behavior of hydrogen isotopes. At last, some suggestions were given for future fusion reactor, including preservation, loading and improvement.

Experimental

Li_2TiO_3 pebbles with a diameter of approximately 1 mm were provided by School of Materials Science and Engineering, University of Science and Technology Beijing, and the characteristics of the pebbles were evaluated by Ming Hong et al. [13]. Some details of experimental conditions are listed in Table 1. In order to clarify the correlation between pressure and vacuum-annealing defect, the pebbles were annealed under the different pressures of approximately 10 Pa, 10^{-1} Pa, 10^{-3} Pa and 10^{-4} Pa at 550 °C for 1 h. The colored Li_2TiO_3 pebbles were annealed at temperatures of 100, 200, 350 and 550 °C in air to demonstrate the correlation between color change and the density of vacuum-annealing defects. As to investigate the mechanism of vacuum-annealing defects, the following treatments have been performed. The sample A was annealed in air at 800 °C for 1 h and then transferred into vacuum immediately for heating. Sample B was immerged in water for 6 h. Sample C was exposed in air for 30 days. All the samples were annealed at 550 °C for 1 h under the pressure of 0.1 Pa. The samples were annealed in different atmospheres to investigate the effects of gas on vacuum-annealing defects. As to give some suggestions on loading tritium breeding material of Li_2TiO_3 for future fusion reactor, the samples were annealed at 800 °C in air for 1 h and then exposed in air for different days. After exposing in air, the samples were annealed at 550 °C under the pressure of 0.1 Pa for 1 h to study the concentration of vacuum-annealing defects by ESR. The colored samples together with samples annealed at 800 °C in air were transferred into 10^{5} Pa D_2 gas for absorption. The temperature of D_2 absorption was set at 300 °C to avoid reduction of Li_2TiO_3 by D_2. After absorption 3 h treatment, thermal desorption spectroscopy (TDS) was performed at a heating rate of 10 °C/min from room temperature to 900 °C. The vacuum system is better than 10^{-5} Pa. Deuterium thermal desorption spectra were obtained using a quadrupole mass spectrometer (QMS). X-ray diffraction (XRD) and Raman were performed to investigate the crystalline phase and the details of the crystal structure in Li_2TiO_3 before and after vacuum-annealing. The XRD measurement was performed at a X'Pert X-ray diffractometer made by PANalytical, Holland. This diffractometer with Cu K_α source was used in a 2θ mode, 2θ varying from 10° to 70° with a 0.03° step. Raman spectra were measured over the range from 100 to 1000 cm^{-1} using a Jobin Yvon LABRAM-HR Raman spectrometer. The spectra were record with acquisition time of 100 s. Electron spin resonance has been applied to study the defects evolution. The measurement was performed over the range from 298.3 mT to 348.3 mT at a JES-FA200 ESR device made by JEOL, Japan. The ESR peak area represents the amount of defects. It can be obtained by integrate ESR peak twice and was normalized to mass.

Results and discussion

Characterization of vacuum-annealing Li_2TiO_3

The color of Li_2TiO_3 pebbles was found to be changed from white to dark blue (Fig. 1(b)) after annealing at 550 °C for 1 h under the pressure of 0.1 Pa. Then the pebbles were transferred into a tube and annealed in air at 800 °C for 1 h. The color of the samples returned to white again (Fig. 1(c)). This

Table 1 – Some details of experimental conditions.

Sample	Different pressure (heating at 550 °C/1 h)	Different temperature (heating at 0.1Pa/1 h)	Different atmosphere (heating at 550 °C/1Pa/1 h)	Different time exposed in air (heating at 550 °C/0.1Pa/1 h)
Li_2TiO_3	10^{5}, 10, 10^{-1}, 10^{-3}, 10^{-4} Pa	200, 300, 350, 550, 650, 750 °C	Air, D_2, N_2	0, 1, 3, 5, 8, 10, 30 days