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Influence of irradiation defects and atmosphere on luminescence and tritium release from Li_2O

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Abstract

Lithium oxide (Li_2O) is a potential candidate as a tritium breeding material for a fusion reactor blanket. The breeder materials will be exposed to a high irradiation dose during its operation. Therefore, the influence of irradiation-induced defects and radiolysis products on parameters of the tritium release is one of the important R&D issues. Simultaneous measurements of the luminescence and tritium release during the temperature transient under reactor irradiation were conducted using a Li_2O, which was pre-irradiated by the electron accelerator to an absorbed dose of 50 ± 10 MGy. It was found that the irradiation defects in Li_2O introduced by the electron irradiation influence the tritium release and luminescence. The long term conditioning under the certain chemical composition of the sweep gas influenced the luminescence spectrum. Influence of irradiation defects and atmosphere on the tritium release and luminescence emission is discussed. © 1997 Elsevier Science B.V.

1. Introduction

The tritium release kinetic of breeder materials is an important property for the engineering design of a fusion reactor. It was reported elsewhere [1–4], that during the temperature increase a negative peak in the curve of tritium release was observed. Several hypotheses had been put forward in order to explain the reason for this phenomenon: first, by a variation of desorption activation energy with a surface coverage of sample [5]; second, by a strong relationship between the occurrence of the negative peak and water vapor in the recovered sweep gas [3]; third, by an interaction of the tritium with irradiation defects causing a change of the chemical form of tritium [6,7].

The present work deals with the study of a role of irradiation-induced defects in the tritium release behavior. Among the examined and predicted radiation defects and products in Li_2O, the colloidal lithium (Li_n) and quasi-colloidal particles (F_n centers) can combine with tritium in the form of LiT, which decomposes at high temperature (for LiH it is 1223 K [8]). This can significantly affect the tritium recovery from Li_2O. However, it should be taken into account the possible influence of F^+ and F^0 centers on tritium release. In spite of intensive studies of this problem [9–12], the role of F-centers is still not well elucidated.

The preliminary investigations of the influence of irradiation atmosphere on a luminescence spectrum was reported [13] for a Li_2O single crystal. It was difficult to evaluate where the effect of the chemical composition of the sweep gas works, on the surface or in the bulk of single crystal sample. Therefore, the luminescence spectrum in the dependence of irradiation atmosphere was studied using a Li_2O polycrystal, so that the luminescence emission from the bulk should not contribute.

2. Experimental

Lithium oxide single crystal or polycrystalline pellet (TD = 80%) was used for investigation. Simultaneous measurements of the luminescence emission and tritium release from Li_2O were carried out at the 'YAYOI' reactor of the University of Tokyo at temperatures up to 873 K and under controlled atmosphere (N_2 or $N_2 + 1\%H_2$). The

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luminescence from the sample was guided through a quartz lens and a quartz optical fiber to a monochromator, and then was measured by a photon-counting system. Released tritium was detected using an ionization chamber. The experimental facility is shown in Fig. 1.

The polycrystalline Li_2O was used for the study of the dependence of luminescence spectrum on the sweep gas chemical composition. The long term (20 h) conditioning under the certain sweep gas was conducted. The measurements were carried out for the same sample at the same nuclear and geometrical conditions, and only the irradiation atmosphere was the varying parameter: N_2 to $N_2 + 1\%H_2$, and reverse.

Studies of an influence of the irradiation defects on the luminescence and tritium release were carried out using a Li_2O single crystal which had been pre-irradiated by electron accelerator (2.2 MeV, 2.5 μA) to an absorbed dose of 50 ± 10 MGy, at the specimen temperature, T, of 150 ± 20 K. The kinetics of the luminescence emission at 340 nm (F^0 center) and tritium release were measured during the rise of temperature in the range of 303–873 K.

3. Results and discussion

3.1. The effect of atmosphere

The experiments were carried out using a pellet of Li_2O polycrystal. The influence of the atmosphere on tritium release showed the well known phenomenon. The tritium release was immediately accelerated by the addition of 1% H_2 to N_2. However, the luminescence spectrum was not influenced by the change of irradiation atmosphere during the period of 2 h. Therefore, the long term conditioning under the certain sweep gas was conducted. Fig. 2 shows luminescence spectra from Li_2O, which were exposed for 20 h to N_2 or $N_2 + 1\%H_2$ atmosphere at 873 K.

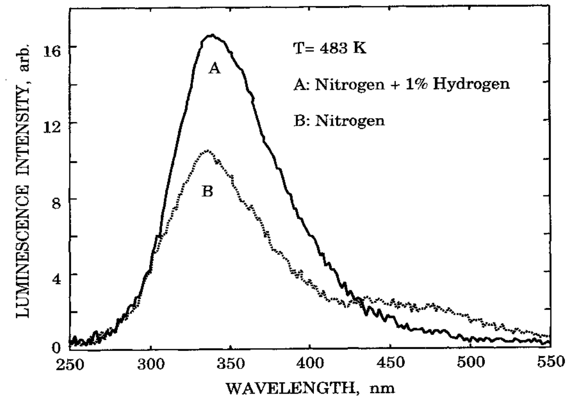

Fig. 2. Luminescence spectra from Li_2O polycrystal at 483 K after 20 h conditioning at 873 K under certain atmosphere: A – $N_2 + 1\%H_2$, B – N_2.

It is clear that the chemical composition of the sweep gas plays a significant role in a surface process. The addition of hydrogen to nitrogen increased the luminescence intensity at 300–400 nm and caused the disappearance of 480 nm peak (F_2 center luminescence affected by OH^- group [13]).

According to Ref. [13], the luminescence spectrum shown in Fig. 3 can be deconvoluted into five emission bands peaked at 4.12 eV (intrinsic defect or impurity), 3.69 eV (F^0 center), 3.27 eV (F^+ center), 2.90 eV (F_2 center) and 2.60 eV (F_2 center affected by OH^- group). The lack of the 480 nm peak in the presence of H_2 in the sweep gas can be explained as follows: the surface OH^- groups is removed due to the reaction with H_2, thus the luminescence at 480 nm caused by the presence of OH^- groups is not emitted.

The difference in the luminescence emission at 300–400 nm can arise from the following reason: in the presence of

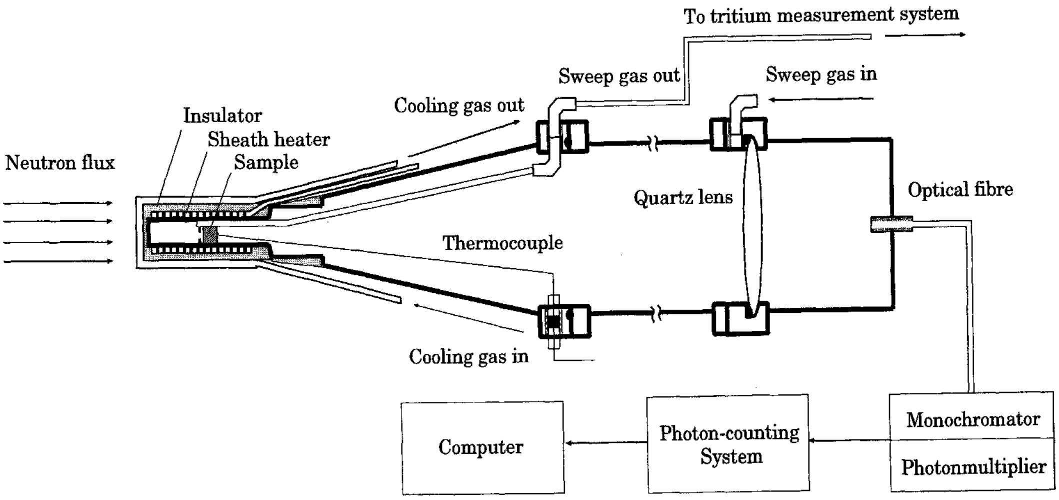

Fig. 1. Scheme of experimental facility for simultaneous measurements of the luminescence and tritium release.

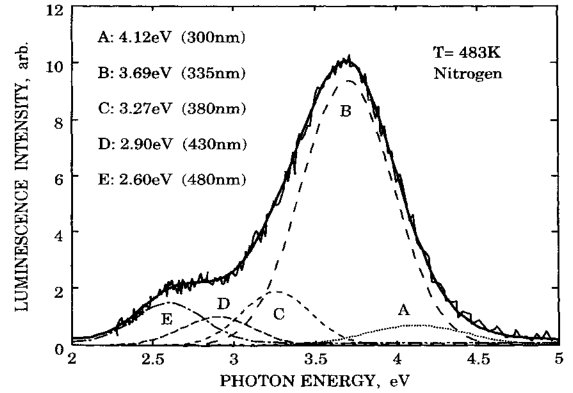

Fig. 3. Luminescence spectrum from Li_2O polycrystal at 483 K after 20 h conditioning at 873 K under the atmosphere of N_2.

OH^- the quenching of F^0 (335 nm) and F^+ (380 nm) can be expected as it was observed in alkali halides [15].

It is well known that impurities can strongly affect the luminescence emission, as well as this can result in the change of the accumulation kinetic of radiation defects and radiolysis products. The oxygen vacancies can be produced on the surface of H_2O vapors due to the reaction of OH^- group with H_2 (from sweep gas). Thus, this can also be a reason for the luminescence dependence on the irradiation atmosphere. The contribution of various emission bands is shown in Table 1. It is possible that OH^- groups cause quenching of F^+ center emission and at the same time increase the luminescence emission at 480 nm working like impurity luminescence centers.

The effect of irradiation atmosphere on luminescence was not observed at temperatures over 573 K. This is reasonable because the strong thermal quenching of the luminescence emission starts with the increase of temperature over 523 K [13].

3.2. The effect of irradiation defects

During the reactor irradiation the luminescence spectrum of Li_2O was found to be consisted of five emission bands at 305, 340, 375, 430 and 510 nm [13]. The 305 nm band is attributed to an intrinsic defect or impurity luminescence. The 340, 375, 430 and 510 nm band are assigned to F-centers luminescence. F-centers are the subject of interest because of their possible interaction with tritium leading to a change of its chemical form. This can cause an influence on tritium release processes.

Table 1
The contribution of integrated intensities of emission bands to the luminescence spectrum of Li_2O polycrystalline pellet at 483 K in dependence on irradiation atmosphere

Emission (eV (nm))	Band contribution (%)	
	atmosphere N_2	atmosphere N_2 + 1%H_2
2.60 (480)	7.9	–
2.90 (430)	5.9	4.7
3.27 (380)	10.6	19.8
3.69 (335)	69.9	71.1
4.12 (300)	5.7	4.4

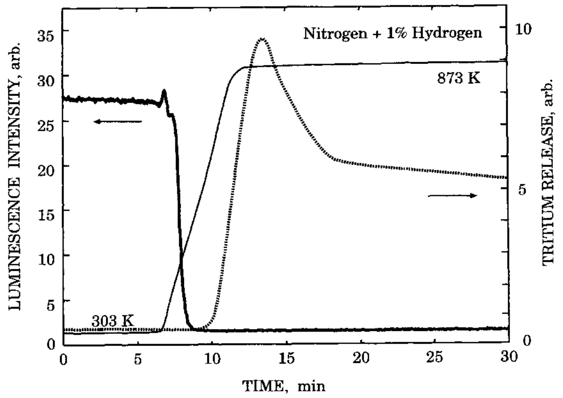

Fig. 4. Simultaneous measurements of luminescence at 340 nm and tritium release from Li_2O single crystal during the temperature transient 303–873 K. Before experiment sample was annealed.

From the experiment dealing with luminescence measurement under He^+ ion irradiation, it was concluded that only the emission at 340 nm should be investigated in detail, because of the phenomenon of 'excess luminescence' at 340 nm during the increase of temperature [6]. This phenomenon was successfully explained [14] by the increase of the concentration of F^0 centers due to the disintegration of colloidal Li. The maximal intensity of the excess luminescence was detected at 623 K.

According to this, the simultaneous measurements of the luminescence emission at 340 nm and tritium release were performed for both the annealed and the pre-irradiated Li_2O single crystals.

Fig. 4 shows the experimental results for the annealed sample. The sample was irradiated at room temperature to the neutron fluence of 10^{17} thermal neutrons/m^2. Afterwards, the temperature was increased to 873 K. At the first stage of tritium release curve the sharp peak is visible. The tritium release rate gradually decreased in time at 873 K. The curve of the temperature dependence of luminescence emission at 340 nm includes also the small thermoluminescence peak at 313–383 K. This peak is probably due to a recombination of F^0 and F^+ centers. There is not observed the tritium retardation and the excess luminescence for the previously annealed sample. It may be explained by a lower absorbed dose by the sample under reactor irradiation in comparison with ion beam irradiation [14].

Fig. 5 shows the experimental results for the specimen pre-irradiated by electron accelerator. The procedure of the

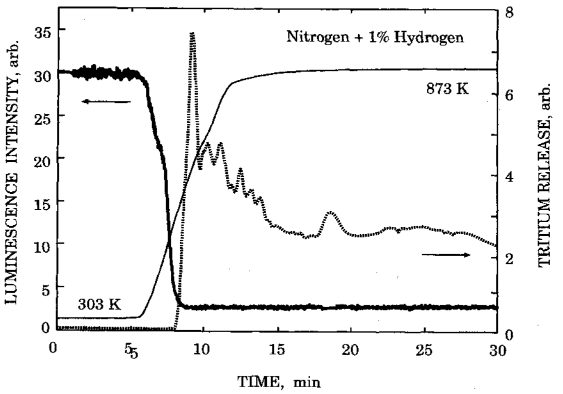

Fig. 5. Simultaneous measurements of luminescence at 340 nm and tritium release from Li_2O single crystal during the temperature transient 303–873 K. Before experiment sample was pre-irradiated by electron accelerator to absorbed dose up to 50 ± 10 MGy.

experiment was the same as was mentioned above. The most outstanding distinction here is the tritium release curve. First, very sharp peak at lower temperature (650 K) could be due to the larger desorption or diffusion rate of tritium than in the case of annealed sample. The diffusion can be enhanced by an increase of the concentration of lithium vacancies or by a weak interaction of F-centers aggregates with tritium. The desorption of tritium can be accelerated due to the increase of the increase of tritium concentration near the surface layers which arises from the enhancement of the diffusion due to irradiation. The tritium release curve of electron-irradiated sample consists of a lot of small peaks, which could be associated to a tritium trapped at F-centers at different distance from the surface of the sample. These F-centers were considered to be formed from the decomposition of Li colloids or F-center aggregates.

The luminescence emission curve did not carry any marker of an 'excess luminescence'. It is reasonable enough, because the effective dose for the formation of Li colloids by the electron irradiation was found to be approximately 100 MGy [14]. As the absorbed dose was estimated at 50 ± 10 MGy, then the formation of Li quasi-colloids or F-center aggregates in the sample can be realized. It seems to be right because small thermo-luminescence peak centered at 443 K cannot be due to isolated F^0 and F^+, but it is the result of a disintegration of F-center aggregates and following recombination of simple F-centers.

It could be summarized that the F-center aggregates do not influence the tritium release, but the F-centers formed during their thermal disintegration can affect it.

Thus discussed, preliminary results showed that the tritium release and the luminescence emission are affected by irradiation defects. In order to make clear this influence and to understand its mechanism, further investigations should be focused on the effect of irradiation dose on the tritium release and the luminescence emission.

4. Conclusions

By simultaneous measurements of the tritium release and luminescence emission from Li_2O, it was found that the interaction of irradiation-induced defects with tritium can take place.

It was confirmed that the irradiation atmosphere influences the luminescence spectrum. It can be expected that there are various kinetics for the accumulation of irradiation defects and radiolysis products which are dependent on the irradiation atmosphere.

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