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In situ luminescence measurement at high temperature from Li_2O under neutron irradiation [1]

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Abstract

During reactor irradiation of Li_2O, the defects are introduced by neutrons, tritons and helium ions produced by $^6Li(n, \alpha)^3H$ reactions, and γ-rays. It is well known that the radiation defects influence the tritium release process. The in situ luminescence emission (LE) measurements have been performed for Li_2O single crystal at the research reactor 'YAYOI' of the University of Tokyo in order to study the behavior of radiation defects under various conditions (temperature, sweep gas chemical composition and neutron spectrum). The LE was observed at the wavelength from 250 to 600 nm at 298–873 K. The luminescence spectra were found to consist of five emission bands. The luminescence emissions at 340 nm (3.65 eV), 375 nm (3.31 eV) and 430 nm (2.88 eV) were assigned to the F^0, F^+ and F_2 centers, respectively. The emission band at 510 nm (2.43 eV) was thought to be due to the F_2 center affected by a hydroxide group. The origin of the luminescence band at 305 nm (4.06 eV) could be related to an intrinsic defect or impurity luminescence. A mechanism of the defects creation and the luminescence emission is discussed. © 1997 Elsevier Science B.V.

1. Introduction

Li_2O is one of the candidates as a tritium breeding material for a fusion reactor blanket. The materials exposed to the neutron irradiation suffer defects production via two routes: direct collisions with atoms and nuclear reactions after capture of neutrons by the nuclei. Thus, the creation of vacancies and interstitials in Li_2O is caused by neutrons, tritons (2.7 MeV) and helium ions (2.1 MeV) produced by the $^6Li(n, \alpha)^3H$ reactions [1]. The production of F-centers in the Li_2O polycrystal by γ-irradiation was detected by the methods of thermo-luminescence and chemical scavengers [2]. Thus, a contribution of γ-rays to the creation of defects should be taken into account. The formation and recovery of various types of irradiation-induced defects in Li_2O were studied by in situ ion conductivity [3] and in situ luminescence measurement [4–6] methods. It was observed that F^0 and F^+ centers affect the diffusion and trapping processes of tritium [3,5,7]. Therefore, as a first step to elucidate this relationship, the behavior of radiation defects was studied by the in situ luminescence measurement under reactor irradiation at high temperatures under sweep gas of various chemical compositions.

2. Experimental

A single crystal of Li_2O was used for the investigation. Before irradiation a specimen was annealed at 773 K for several hours in an inert atmosphere. The sample was irradiated in the temperature range 298–873 K in a research reactor 'YAYOI' of the University of Tokyo with a flux up to 10^{10} neutrons/cm^{2}s of fast (about 1.3 MeV) or thermal neutrons using a sweep gas of various chemical compositions (N_2, $N_2 + 1\%H_2$). It was considered that chemical composition of the sweep gas, particularly H_2, can play an important role in Li_2O surface nature at high temperatures. The experimental facility is shown in Fig. 1.

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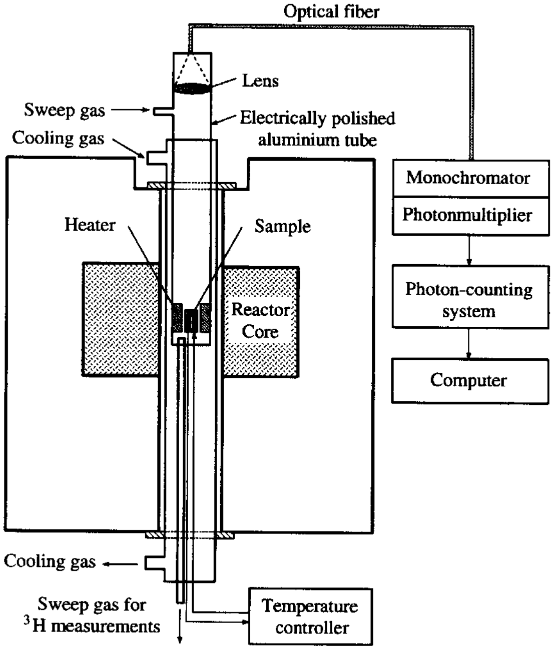

Fig. 1. Scheme of experimental facility.

The luminescence from the sample was guided through an aluminum tube, a quartz lens and a quartz optical fiber to a monochromator, and then was measured by a photon-counting system. In Ref. [4] is given the detailed description of the system for the in situ luminescence measurement using the 'YAYOI' reactor. Observed luminescence spectra were corrected by the detection efficiency of the system, which was determined with calibrated deuterium and tungsten halogen lamps. The calibration was performed by placing the light source in the same position as the sample during the experiment. By this means the spectral response of the whole measurement system was evaluated.

The in situ luminescence measurement was performed for LiOH pellets in order to evaluate its contribution to the luminescence spectrum of Li_2O.

3. Results and discussion

3.1. The luminescence bands assignment

The luminescence spectra were taken during the stepwise change of the temperature, when the LE reached a steady state. At temperatures above 373 K, the measurement was carried out after 2–3 min, when the temperature of the sample became constant. The emission intensity was found constant during measurements with the exception of the low temperature range 298–373 K, when it gradually decreased. For example, at 298 K the luminescence intensity decreased by 25% in the initial 30 min of irradiation and by 10% in the following 30 min. Therefore, at low temperature, a spectrum was recorded 30 min after the time at which the temperature of the specimen reached a constant value.

The luminescence emission was observed at wavelengths from 250 to 600 nm. The analysis of the obtained luminescence spectra was done according to the data of the in situ luminescence observations for Li_2O under reactor irradiation at room temperature [4], under ion beam irradiation at high temperatures [5], and under γ-ray irradiation at 77–298 K [6]. In addition, the computer simulation by Shluger and Itoh [8] was taken into account. The positions of peaks changed with temperature but did not exceed 5 nm. So, the position of the peak at room temperature is used in the present paper. Five LE bands at 305, 340, 375, 430, and 510 nm were determined. In Fig. 2, a luminescence spectrum of Li_2O is represented, which graphically demonstrates the determined emission bands. The half-bandwidth depended on the sample temperature and fell in the 27–35 nm range for the 305, 340, 375 and 430 nm bands and in the 40–50 nm range for the 510 nm band.

The observed bands were assigned in the following way: 340 nm to F^0 center, 375 nm to F^+ center, 430 nm to F_2 center and 510 nm to F_2 center affected by the OH^- group. The origin of the 305 nm band is thought to be related to the intrinsic defect or impurity luminescence.

The reasons for these assignments are as follows: The emission band at 300 nm was observed under γ-ray irradiation at 77–298 K [6]. It was suggested that this band can be due to the intrinsic defect or impurity luminescence. Since the position of 305 nm (under reactor irradiation) and 300 nm (under γ-ray irradiation) bands is almost the same, it seems likely that they are identical in origin as mentioned above.

From the computer modeling of the atomic structure and electronic transition of F-centers [8], the 430 nm peak was assigned to the F_2 center luminescence. In addition, the absorption band at 375 nm was observed in neutron-irradiated Li_2O by Uchida et al. [9] and attributed to the F_2 center. According to the Franck–Condon principle, the Stokes shift is valid between the absorption and emission

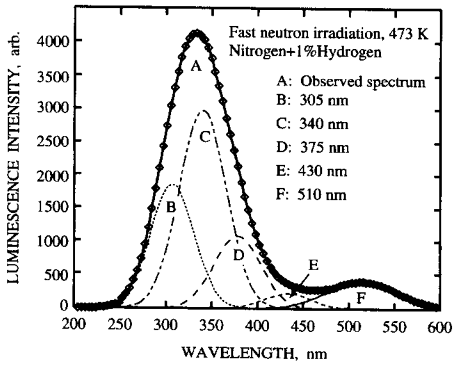

Fig. 2. Luminescence spectrum from an Li_2O crystal under fast neutron irradiation at 473 K.

energies. Thus, it is suggested that the 430 nm peak is due to the F_2 center. The luminescence emission of F_2 centers was also observed under γ-ray irradiation [6].

The formation of F^+ centers and F-center aggregates was investigated by optical absorption and electron-spin resonance methods [9–11]. The assignment of 340, 375, and 510 m bands was conducted based on in situ luminescence measurements [4,5], where these bands were attributed to F^0, F^+ and LiOH, respectively. From the in situ luminescence measurement under ion beam irradiation by Asaoka et al. [5], it was suggested that the 510 nm band is due to the hydroxide on the surface of Li_2O. This was concluded from the sensitivity of the recovery behavior of this band to the thermal treatment of the sample. However, we suggest another interpretation of the origin of the 510 nm band. It should be stressed that under reactor irradiation, the luminescence in the Li_2O crystal is emitted from the whole sample — from the surface and bulk. In contrast to that, the luminescence from the surface layers of the sample can be detected under ion beam irradiation (for instance, the penetration depth of 1 MeV He^+ ion in Li_2O is calculated to be 3.24 μm). Thus, the contribution of LiOH, typically precipitated on the surface of Li_2O, was evaluated by the comparison between the luminescence spectra of LiOH and Li_2O, which were measured at room temperature. The weaker intensity of the luminescence emission was detected at wavelengths of 400–600 nm from the LiOH in comparison with one from Li_2O. Consequently, the 510 nm band originates from the surface and bulk of the Li_2O crystal. There is some evidence that impurities may be important in the process of the relaxation of excited F-centers [12]. In the presence of impurities, an excited electron of defect can be transferred to the lower excited state due to the non-radiative decay. In such a manner two emission bands originating from F-centers can be expected. In the case of Li_2O this process can be realized for the F_2 center, because the 430 nm and 510 nm bands show a similar temperature dependence (Section 3.2), as well as that they are alongside each other in the LE spectrum. Thus, it is suggested that the 510 nm band is related to the F_2 center luminescence affected by the surface and bulk OH^- groups.

The mechanism of the defects creation and LE will be discussed in Section 3.3.

3.2. Dependence on irradiation parameters

The intensity of the luminescence emission was proportional to the neutron flux in the temperature range 373–873 K. At temperatures below 373 K, the intensity gradually decreased during the irradiation, and the neutron flux was higher as it reduced faster. The luminescence spectrum was strongly dependent on temperature (Fig. 3). An Arrhenius plot of the luminescence intensities (Fig. 4) shows that rapid thermal quenching of LE started from 473 K. The emission intensity of the 305 nm band diminished more rapidly in comparison with the other emission bands.

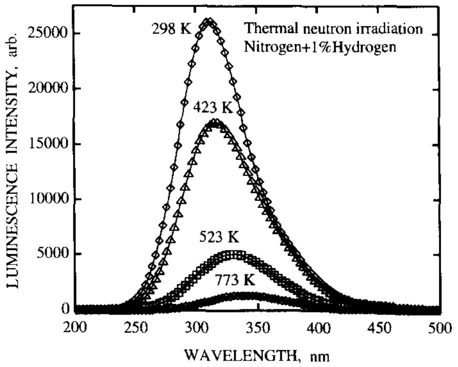

Fig. 3. Temperature dependence of the luminescence emission spectrum of the Li_2O crystal.

At temperatures above 673 K, the luminescence was observed mainly from the F^0 (340 nm) and F^+ (375 nm) centers. The reasons for these phenomena will be explained by the mechanism of LE in Section 3.3.

The luminescence emitted by thermal neutron irradiation was greater than that by fast neutron irradiation. It can be explained by the different cross section of the neutron–lithium reaction for fast and thermal neutrons. More effective production of high energy tritons and α-particles by thermal neutrons causes a more effective electronic excitations; as a result, the intensity of the luminescence emission is greater under thermal neutron irradiation than under fast neutron irradiation. A difference was found in the contribution of emission bands to the luminescence spectrum in the case of fast and thermal neutron irradiations (Figs. 4 and 5). The 305 nm band at 298–473 K gave larger and the 510 nm band at 423–573 K smaller contributions to the luminescence spectra in the case of thermal neutrons. The contribution of F^+ center to the luminescence spectrum at 673–873 K was larger under fast neutron irradiation. The effect of the neutron spectrum was caused by the difference of the efficiency of defects production under fast and thermal neutron irradiations. It has been determined [9] that the efficiency of the defects creation in Li_2O by the collision of fast neutrons is about

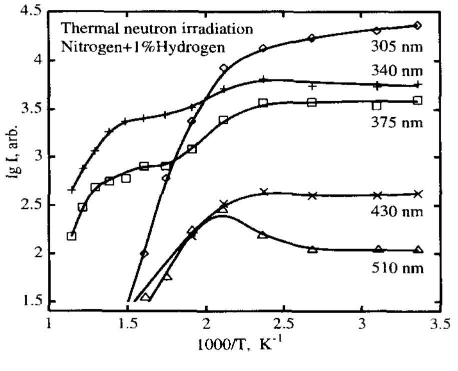

Fig. 4. Arrhenius plot of the luminescence intensities.

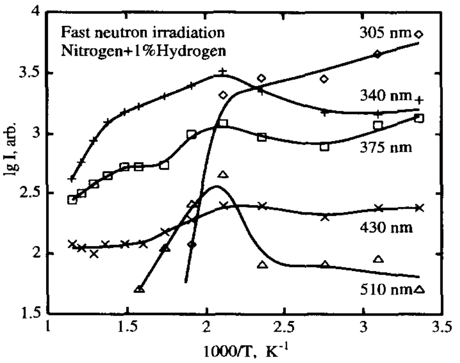

Fig. 5. Arrhenius plot of the luminescence intensities.

five times larger than that of the ^{6}Li(n, α)^{3}H reaction. The concentration of defects can play an important role in the process of the luminescence emission. It has been reported [13] that when the F-centers are isolated, their luminescence efficiency is high. Consequently, it is reasonable that the contribution of the various emission bands is dependent of the neutron spectrum. However, it is difficult to evaluate the effect of neutron spectrum on each luminescence band only from the luminescence spectra. The problem could be solved by the study on the luminescence emission from the samples with various ^{6}Li:^{7}Li ratios. It allows to evaluated the contribution of thermal neutrons and γ-rays to the luminescence emission. Since the cross section of the reaction of thermal neutrons with ^{7}Li nuclei is almost 1000 times smaller than that with ^{6}Li nuclei, the luminescence in Li_2O containing only the ^{7}Li isotope will be mostly emitted by γ-rays, and the contribution of thermal neutrons to the excitation process can be neglected.

An influence on the luminescence emission spectrum of the sweep gas chemical composition was observed in the case of fast neutron irradiation. The addition of 1% H_2 to N_2 decreased the luminescence intensity by 25–30%. However, that did not change a contribution of emission bands to the luminescence spectrum and a temperature dependence of defects behavior. It was presumed that a hydrogen atom diffused into the bulk of the sample and reacted with a hole defect O^-. This caused the decreasing of the LE, because the hole is involved in recombination processes with following LE, which will be discussed in the next section. Further experiments will be required, because there is a possibility that the surface will be modified by the chemical composition of the sweep gas in a longer time than the several hours of the experiment.

3.3. The mechanism of luminescence

The excitation energy can he dissipated through any of four principal channels [12]: (1) emission of luminescence, (2) phonon creation, (3) production of lattice defects such as vacancy–interstitial pair and (4) transfer energy to some existing imperfection. The relative importance of these channels depends on temperature, the material and its state of impurity.

The annihilation of electron–hole pairs $(O^-e^-)^*$ can go by the accompaniment of photon emission in the following ways [14]:

$$(O^-e^-)^* + V_a \to O_i^- + (F^+)^* \to F^+ + O_i^- + h\nu_{375}, \tag{1}$$

$$(O^-e^-)^* + V_a \to O_i + (F^0)^* \to F^0 + O_i + h\nu_{340}, \tag{2}$$

$$(O^-e^-)^* + F^+ \to O_i^- + (F^0)^* \to F^0 + O_i^- + h\nu_{340}, \tag{3}$$

$$(O^-e^-)^* + F_2^+ \to O_i^- + (F_2)^* \to F_2 + O_i^- + h\nu_{430}. \tag{4}$$

Here O^- is a hole, V_a is an oxygen vacancy, O_i^- is an interstitial hole, O_i is an interstitial atom, and F_2^+ is adjacent to F^0 and F^+ centers.

The creation of F^+ centers proceeds through the electron–hole (e–h) recombination followed by trapping of an electron by an anion vacancy (Eq. (1)). When the recombination of an e–h pair proceeds and an anion vacancy traps two electrons (Eq. (2)) or an F^+ center traps an electron (Eq. (3)), the F^0 center is produced.

In the case of nearby F^0 and F^+ centers, the capture of an electron by an F^+ center leads to the production of the excited F_2 center (Eq. (4)), the relaxation of which is accompanied by LE at 430 nm. If the relaxation process is affected by OH^-, the emission band appears at 510 nm.

In addition, the excited state of defects can be induced by energetic tritons and helium ions as well as by γ-ray irradiation (Compton scattering). However, the main contribution to the luminescence emission is due to the energy transfer from e–h pairs to the luminescent defects. Also a recombination of F-centers with hole defects induces LE. This process is dominant at high temperatures due to the increase of hole mobility and probability of the liberating of an electron from the trap [13].

As was mentioned in Section 3.2, the thermal quenching of LE bands started from 473 K and the quenching of the 305 nm band was the faster of all. The quenching of the LE bands can be explained by non-radiative relaxation through a thermal activation process competing with radiative relaxation [15]. At high temperatures, the non-radiative relaxation of luminescent defects was considered to become dominant. Processes described by Eqs. (1) and (2) strongly depend on the concentration of oxygen vacancies and by Eqs. (3) and (4) are determined by the concentration of F^+ centers.

The modeling of defects production in Li_2O under ion beam irradiation was made by Asaoka et al. [16]. In their experiments, it was observed that the predominant formation of F^0 centers occurs at high temperatures and of F^+ centers at low temperatures. However, the luminescence bands of F^0 and F^+ centers in Li_2O under neutron irradiation were detected at 293–873 K. The difference in the behavior of F-centers between neutron and ion beam irradiations could be explained by higher electronic excitations and displacement damage induced by the He^+ ion than those by neutron. In our experiments, the dose rate was evaluated to be up to 2.5 Gy/s. From the other side, the dose rate during the ion irradiation can reach as much as 500 kGy/s. Thus, the concentration of irradiation defects produced by ion irradiation is higher than that created under reactor irradiation. In addition, it should be stressed that the formation of F-center aggregates and colloidal Li proceeds under ion irradiation [17]. According to the radiation dose of the reactor irradiation in our experiments, the formation of isolated F-centers takes place [2]. Thus, the dose rate is the main reason for the difference in the behavior of F-centers between neutron and ion beam irradiations.

According to the mechanism of luminescence emission and defects production in Li_2O proposed by Asaoka et al. [5,16], the F^+ centers are produced from excited Li_2O with the partners of peroxy species (Li_2O_2) and F^0 centers are produced with the partners of O_2. It was concluded that the luminescence emission is mainly associated with the production of irradiation defects [16]. However, we suggest that the LE and defects formation mainly occurs by the relaxation of the e–h pair, which can proceed by various ways (Eqs. (1)–(4)). The processes described by Eqs. (1) and (2) are dependent on the concentration of oxygen vacancies and on the density of electronic excitations, while those described by Eqs. (3) and (4) are dependent on the concentration of F-centers, which are generated by reactions (Eqs. (1)–(3)), and are considered to give a small contribution to the luminescence spectrum, especially at high temperatures, when the recombination of radiation defects takes place.

The recent investigation [17] of the phenomenon of 'excess luminescence' [16] under ion beam irradiation supported our mechanism of the luminescence emission in Li_2O under neutron irradiation. It was shown, that this phenomenon is caused by the thermo-dissociation of colloidal Li, which results in the creation of F-centers and oxygen vacancies. Formed oxygen vacancies capture electrons during the irradiation and form excited F-centers, whose relaxation gives the 'excess luminescence'. This supports our mechanism of LE and proves that the LE due to the recombination of radiation defects does not give any significant contribution to the luminescence emission spectrum.

4. Conclusions

As a first step to elucidate defects behavior under reactor irradiation and their influence on tritium release process from Li_2O, the in situ luminescence measurements were carried out for single crystal under reactor irradiation at high temperatures.

(1) A complex broad luminescence peak was observed and five emission bands were determined at 305 nm (4.06 eV), 340 nm (3.65 eV), 375 nm (3.31 eV), 430 nm (2.88 eV) and 510 nm (2.43 eV). The luminescence emissions at 340, 375 and 430 nm were assigned to the F^0, F^+ and F_2 centers, respectively. The 510 nm band was suggested to be F_2 center luminescence affected by hydroxide group. The origin of the 305 nm band could be related to the intrinsic defect or impurity luminescence.

(2) The mechanism of the defect creation and the luminescence emitted in Li_2O by neutron irradiation was suggested.

(3) The luminescence emission strongly depended on temperature. The main contribution to the luminescence spectrum at high temperatures was given by F^0 and F^+ centers.

(4) The luminescence emitted by thermal neutron irradiation was greater than that by fast neutron irradiation. The contribution of emission bands to the luminescence spectrum was affected by the neutron spectrum.

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