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Production behavior of irradiation defects in lithium silicates and silica under ion beam irradiation

Kimikazu Moritani [a], Shiro Tanaka [b], Hirotake Moriyama [c,*]

[a] Department of Nuclear Engineering, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan
[b] Department of Hydrocarbon and Energy Chemistry, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan
[c] Research Reactor Institute, Kyoto University, Kumatori-cho, Sennan-gun, Osaka 590-0494, Japan

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Abstract

For the performance assessment of fusion reactor solid breeder materials, the production behavior of irradiation defects in the ternary lithium ceramics of Li_2SiO_3 and Li_4SiO_4 was studied by an in situ luminescence measurement technique under ion beam irradiation of H^+ and He^+. For comparison the measurement was also performed with vitreous SiO_2. The temperature dependence of the luminescence intensity and the transient behavior of the luminescence intensity on temperature changes were measured for kinetic aspects of the involved reactions, and the production mechanisms and kinetics of the irradiation defects in these lithium ceramics were discussed. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

For the performance assessment of fusion reactor blanket systems, the effects of irradiation on the tritium release behaviors and microstructural changes of lithium ceramics are particularly important. In spite of its importance, however, little is yet known on the mechanism of these effects [1,2].

For a clearer understanding, we have studied the production behavior of irradiation defects in some candidate lithium ceramics by an in situ luminescence measurement technique under ion beam irradiation. In Li_2O, it has been confirmed that the F^+ center (an oxygen vacancy trapping an electron) and the F^0 center (an oxygen vacancy trapping two electrons), which are commonly observed in ionic compounds, are formed by irradiation [3,4]. Similarly, the irradiation defects of oxygen vacancies are produced in Li_2SiO_3 and Li_4SiO_4 [5,6]. These defects are considered to play an important role in the tritium behavior [2].

In our recent studies [7,8], the production behavior of irradiation defects in the ternary lithium ceramics of Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3 was studied, and the production mechanism of irradiation defects in these materials was found to be rather similar to that in Li_2O. For comparison, the present study deals with kinetic aspects of the production behavior of irradiation defects in Li_2SiO_3, Li_4SiO_4 and SiO_2. The transient behavior of luminescence intensities for temperature changes was measured and the results were analyzed to determine the values of kinetic parameters of the involved reactions.

2. Experimental

The lithium ceramics of Li_2SiO_3 and Li_4SiO_4 were prepared by solid-state reactions. Powders of SiO_2 of reagent grade from Nacalai Tesque, were milled with Li_2CO_3 in stoichiometric amounts and calcined at 1223 K for 8 h. The formation of each compound was confirmed by X-ray diffraction. The contents of Li_2SiO_3 in Li_4SiO_4 and of Li_4SiO_4 in Li_2SiO_3 were found to be negligible (<1%) by diffraction peak analysis. Pellet-type

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[*] Corresponding author. Tel.: +81-724 512 424; fax: +81-724 512 634.
E-mail address: moriyama@rri.kyoto-u.ac.jp (H. Moriyama).

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samples of 10 mm in diameter and about 1 mm in thickness were sintered at 1423 K for 8 h. A vitreous SiO_2 (T-1030) of the same size was obtained from Toshiba Ceramics.

A 2 MeV H^+ or He^+ ion beam, accelerated with a Van de Graaff accelerator, was led to the target sample at 90°. The size of the ion beam was about 3 mm in diameter and its current was monitored. The luminescence from the target sample was led to monochromaters, Ritsu MC-20N, and counted with photomultipliers, Hamamatsu R585. The temperature of the sample holder was controlled with an electric heater and a thermocouple, while another thermocouple was attached to the sample surface to monitor its temperature.

3. Results and discussion

3.1. Luminescence bands

Fig. 1 shows typical luminescence spectra of Li_2SiO_3, Li_4SiO_4 and SiO_2 under He^+ ion beam irradiation. For comparison, the ordinate represents luminescence intensity normalized to the beam current of 1 μA; the peak heights have been observed to be proportional to the beam current and then all of the spectra in the present study are corrected with the beam current. Similar spectra were also observed under H^+ irradiation. As shown in Fig. 1, the observed luminescence spectra are decomposed into a number of luminescence bands, namely 330, 380, 420 and 490 nm for Li_2SiO_3, 350, 420, 470 and 520 nm for Li_4SiO_4, and 280, 450 and 490 nm for SiO_2. For the decomposition, following the manner in the previous study [7], energy-based Gaussian functions were taken for all the luminescence bands and the peak heights and positions were determined. For a proper convergence, the peak width has been assumed to be given by an empirical correlation that $y = cx^{-2}$, where y denotes the peak width in eV, x the peak position in eV and c is the constant.

Although no clear difference in the luminescence spectra between Li_2SiO_3 and Li_4SiO_4 has been observed in the previous studies [5,6], the spectra of Li_2SiO_3 and Li_4SiO_4 are found to differ from each other in the present study. By considering the higher purity (>99%) of the presently used samples which has been confirmed by X-ray diffraction, however, the present results are believed to be more reliable. The previous results are thus considered to show some contamination of Li_4SiO_4 with a small amount of Li_2SiO_3.

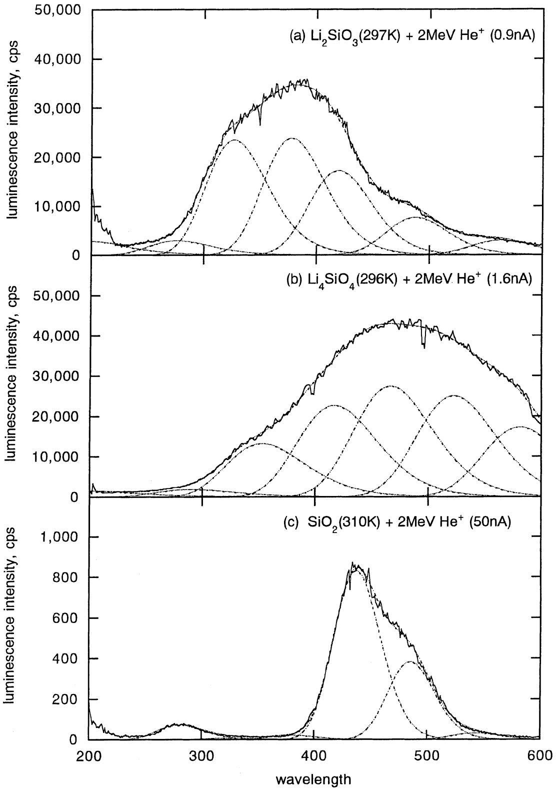

Fig. 1. Typical luminescence spectra of Li_2SiO_3, Li_4SiO_4 and SiO_2 under He^+ ion beam irradiation. The ordinate represents luminescence intensity normalized to the beam current of 1 μA. Curves represent the results of decomposition as described in 3.1.

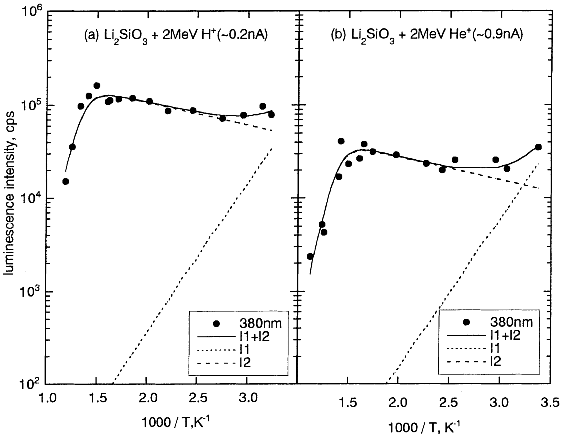

Fig. 2. Arrhenius plots of luminescence intensity of Li_2SiO_3 under (a) H^+ and (b) He^+ irradiations. The ordinate represents luminescence intensity normalized to the beam current of 1 μA. Marks are experimental and curves represent the least-squares fits of the data to Eqs. (4) and (5) as described in 3.4.

Figs. 2 and 3 show the Arrhenius plots of the luminescence intensity at fixed bands for Li_2SiO_3 (380 nm) and Li_4SiO_4 (470 nm), respectively. As shown in Fig. 2 for Li_2SiO_3, the intensity increases with temperature and reaches the maximum value at around 650 K and then decreases above the temperature. In Fig. 3, a similar

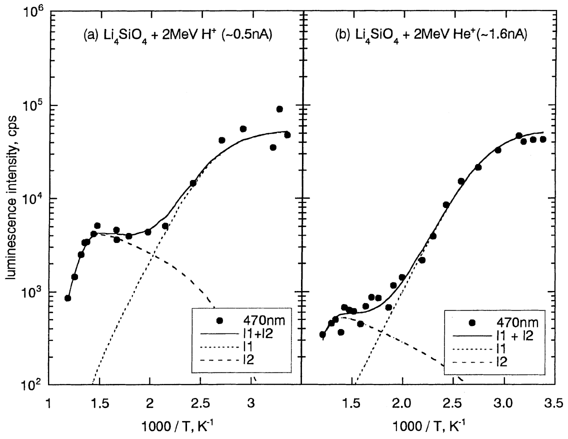

Fig. 3. Arrhenius plots of luminescence intensity of Li_4SiO_4 under (a) H^+ and (b) He^+ irradiations. See also Fig. 2 caption.

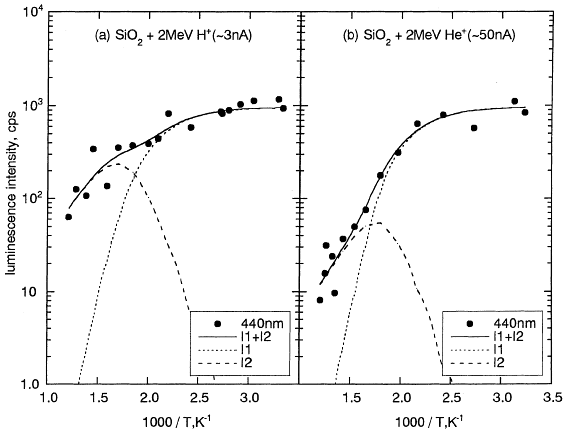

Fig. 4. Arrhenius plots of luminescence intensity of SiO_2 under (a) H^+ and (b) He^+ irradiations. See also Fig. 2 caption.

trend is also recognized for Li_4SiO_4 though it is not so significant. Thus the observed temperature dependences are not monotonic, and at least two different sources of the luminescence are considered to be present in these ceramics. A similar situation is also considered to hold for SiO_2 as shown in Fig. 4.

3.2. Temperature-transient behavior

Fig. 5 shows a typical result of the temperature-transient behavior of luminescence intensity in Li_2SiO_3. For a temperature increase, the luminescence intensity first increases, thereafter it decreases and settles down to an equilibrium value. This phenomenon is the so-called excess luminescence as reported for Li_2O [4] and for other lithium ceramics of Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3 [8]. In the case of Li_2O [4], the excess luminescence was observed to depend on the irradiation time before the temperature change and increase with increasing irradiation time. Also, it was found that the excess luminescence intensity saturated at some equilibrium value which was roughly proportional to the second power of the beam current. It was then suggested that the second-order reactions of irradiation defects were involved in the reaction mechanism. In the case of the ternary ceramics such as Li_2TiO_3, on the other hand, it was found that the excess luminescence was little dependent on the irradiation time except for the very early stage of irradiation and that the equilibrium condition was attained very rapidly for the involved reactions [8].

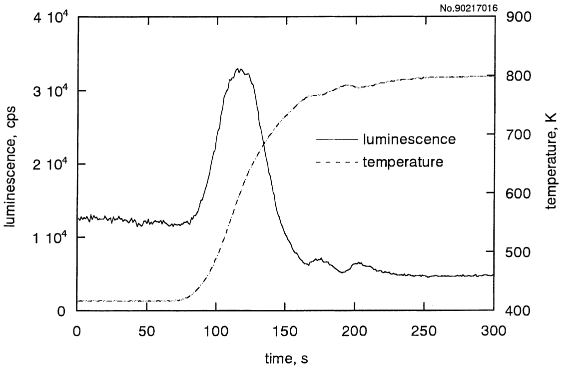

Fig. 5. Temperature-transient behavior of luminescence intensity at 380 nm for Li_2SiO_3 irradiated with 2 MeV H^+ ions of 5 nA. Irradiation time before a temperature increase is 300 s.

The present results of Li_2SiO_3 and Li_4SiO_4 are found to be a little different from those of Li_2O and of Li_2TiO_3, Li_2ZrO_3 and Li_2SnO_3. In Fig. 6, the excess luminescence is plotted as a function of irradiation time before the temperature increase. It can be seen that the excess luminescence decreases with increasing irradiation time when the irradiation temperature is kept high, while it is

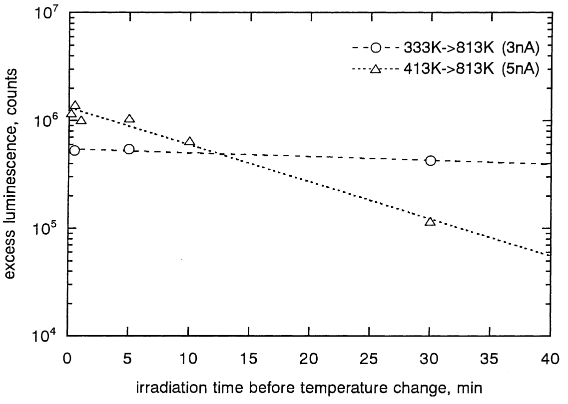

Fig. 6. Dependence of excess luminescence on irradiation time for Li_2SiO_3 irradiated with 2 MeV H^+ ions.

rather constant at lower irradiation temperatures. This indicates that the excess luminescence is associated with the formation of irradiation defects for which some activation energy is needed. At lower temperatures, such a defect could not be formed by irradiation before the temperature increase, and any irradiation history might not be observed. At higher temperatures, on the other hand, the defect will be formed before the temperature increase and, because of the effect of saturation, its formation following the temperature change will decrease with increasing irradiation time.

3.3. Production mechanism of irradiation defects

It is important to address the observed luminescence bands to respective sources. However, such an information is still lacking for lithium silicates, and extensive studies of SiO_2 are referred for the interpretation of the observed phenomena and for the suggestion of a possible production mechanism of irradiation defects.

In the case of SiO_2, there have been reported two types of irradiation defects [9]. One is the oxygen-deficiency-related defects of the so-called E′ centers and some variants of oxygen deficiency centers (ODCs), and the other the oxygen-excess-related defects such as the non-bridging oxygen hole centers and the peroxy radicals. As for the luminescence of irradiation defects, it is known that the luminescence of ODCs is observed at the UV region around 2.7 eV (460 nm) and 4.4 eV (280 nm) while that of the others like the non-bridging oxygen hole centers is observed at rather low photon energy region. Thus the presently observed luminescence from SiO_2 which is centered at 440 nm can be attributed to ODCs. Also, by considering a structural analogy between SiO_2 and silicates, the formation of similar type irradiation defects may be expected for lithium silicates. According to recent studies of silica, the luminescence intensity is linearly dependent not only on electronic excitation rate [10] but also on displacement rate [11], and it is reasonable to assume that the luminescence comes from the relaxation process of newly formed ODCs trapping electrons.

In our previous study [6], it has been reported that the observed temperature-dependent behavior is associated with the formation of the oxygen vacancy centers in the LiO_n polyhedra like ODCs in SiO_2 which is accompanied with the incorporation of the removed oxygen atom into an adjacent SiO_4 tetrahedra to form a peroxy linkage. In general, however, the formation of ODCs is not necessarily accompanied with the formation of peroxy linkages but of oxygen interstitials. Considering these two processes, the following production mechanism of irradiation defects in $Li_{2n}SiO_{n+2}$ $(n = 0, 1, 2)$ can be suggested:

$$Li_{2n}SiO_{n+2} \rightarrow Li_{2n}SiO^*_{n+2} \tag{1}$$

$$Li_{2n}SiO^*_{n+2} \rightarrow ODC + O_i + hv \tag{2}$$

$$Li_{2n}SiO^*_{n+2} \rightarrow ODC + (\text{–O–}) + hv \tag{3}$$

Reaction (1) represents the production of an excited $Li_{2n}SiO_{n+2}$ ($Li_{2n}SiO^*_{n+2}$) by ion beam irradiation, and reactions (2) and (3) represent the formation of an ODC accompanied with the formation of an oxygen interstitial (O_i) and a peroxy linkage (–O–), respectively. There are two types of ODCs of the relaxed ODC(I) and the non-relaxed ODC(II) for SiO_2 [9], and then some differences may be expected for ODCs in reactions (2) and (3). Because of the lack of information available, however, any distinction of ODCs is not made in the present study. Such a distinction is not so easy since ODCs are diamagnetic and thus invisible to electron paramagnetic resonance (EPR) techniques.

Reaction (3) requires some thermal activation and will take place at high temperatures since the moved oxygen atom is incorporated into a peroxy linkage. This is the reason why the luminescence of reaction (3) is observed at high temperatures. Reaction (3) is also consistent with the observation in which the excess luminescence decreases with increasing irradiation time at higher temperatures since the formation of peroxy linkages is saturated by irradiation before the temperature change.

3.4. Determination of kinetic parameters

It is interesting and important to obtain the rate constants of reactions involved in the production of irradiation defects. Based on the suggested reaction scheme, the observed temperature dependence of the luminescence intensity can be analyzed.

Following the reaction scheme, the observed luminescence intensity I is expressed as

$$I = I_1 + I_2 = k_1[Li_{2n}SiO^*_{n+2}] + k_2[Li_{2n}SiO^*_{n+2}], \tag{4}$$

where I_1 and I_2 are the luminescence intensities, and k_1 and k_2 are the rate constants of reactions (2) and (3), respectively. The lifetime of $Li_{2n}SiO^*_{n+2}$ is assumed to be very short and a steady-state approximation is applied to $Li_{2n}SiO^*_{n+2}$, that is:

$$\begin{aligned} &d[Li_{2n}SiO^*_{n+2}]/dt \\ &\quad = g' - k_1[Li_{2n}SiO^*_{n+2}] - k_2[Li_{2n}SiO^*_{n+2}] \\ &\qquad - \sum_{i \geqq 3} k_i[Li_{2n}SiO^*_{n+2}] = 0, \end{aligned} \tag{5}$$

where g' is the apparent generation rate of $Li_{2n}SiO^*_{n+2}$ by reaction (1) and k_i $(i \geqq 3)$ are the rate constants of the reverse reaction of reaction (1) and of some other non-radiative transition of $Li_{2n}SiO^*_{n+2}$. In order to calculate

Table 1
Optimum parameter values obtained from the analysis of in situ luminescence measurement data

Ceramics	Projectile	$k_2/k_1 = A_2/A_1 \exp[-(E_2 - E_1)/RT]$		$k_3/k_1 = A_3/A_1 \exp[-(E_3 - E_1)/RT]$		$k_4/k_1 = A_4/A_1 \exp[-(E_4 - E_1)/RT]$		g′ (s^{-1})
		$A_2/A_1(-)$	$E_2 - E_1$ (kJ/mol)	$A_3/A_1(-)$	$E_3 - E_1$ (kJ/mol)	$A_4/A_1(-)$	$E_4 - E_1$ (kJ/mol)	
Li_2SiO_3	H^+	1.2×10^6	35.1	1.8×10^6	29.9	4.9×10^{13}	134.2	6.7×10^5
	He^+	7.0×10^5	(35.1)[a]	4.6×10^6	(29.9)[a]	1.8×10^{14}	(134.2)[a]	(6.7×10^5)[a]
Li_4SiO_4	H^+	2.3×10^5	50.7	4.3×10^5	41.1	2.7×10^{13}	153.0	5.4×10^4
	He^+	5.4×10^4	(50.7)[a]	9.9×10^5	(41.1)[a]	1.5×10^{13}	(153.0)[a]	(5.4×10^4)[a]
SiO_2	H^+	9.8×10^6	72.0	3.4×10^3	32.4	1.1×10^{10}	104.1	9.6×10^2
	He^+	2.6×10^6	(72.0)[a]	3.2×10^3	(32.4)[a]	2.1×10^{10}	(104.1)[a]	(9.6×10^2)[a]

[a] Assumed to be the same for both H^+ and He^+ ion irradiations of each ceramic.

the luminescence intensity, the steady-state concentration of $Li_{2n}SiO^*_{n+2}$ is obtained from Eq. (5) and substituted into Eq. (4).

In the present analysis, the obtained data for the temperature dependence of the luminescence intensity are fitted to Eqs. (4) and (5) by least-squares method. The rate constants are assumed to be of the Arrhenius type and hence the pre-exponential term A_i and activation energy term E_i are determined. For a proper convergence, the number of free parameters is reduced as much as possible. The energies needed for the production of $Li_{2n}SiO^*_{n+2}$ and for its reactions are essentially the same in each lithium ceramic. Thus the generation rate per unit deposited energy and the activation energy terms are assumed to be the same in each lithium ceramic irrespective of the different projectile ions of H^+ or He^+. On the other hand, the pre-exponential terms are treated to be different for different projectile ions since different reaction conditions may be expected due to different linear energy transfers. As shown in Figs. 2–4, the observed temperature dependence of the luminescence intensity is well fitted to Eqs. (4) and (5), and the values of kinetic parameters of the involved reactions are obtained as given in Table 1.

As can be expected for the first-order reactions, all the ratios of A_2/A_1, A_3/A_1 and A_4/A_1 are rather independent on the projectile ions. However, it may be found that the A_2/A_1 value for both ceramics is slightly larger for H^+ ions than for He^+ ions. This difference will be explained by considering different linear energy transfers of the projectile ions. As mentioned above, reaction (3) for the formation of the ODCs accompanies the incorporation of the moved oxygen into a peroxy linkage, and it will be reduced when the sites for peroxy linkages are saturated. This is the reason why the different A_2/A_1 values are obtained for different projectile ions. In the case of H^+ ions of the lower linear energy transfer, the specific ionization and hence the local concentration of $Li_{2n}SiO^*_{n+2}$ will be low in the ion tracks and the sites for peroxy linkages are hardly saturated, leading to the higher yield of reaction (3). In the case of He^+ ions, on the other hand, those sites will be more easily saturated and then reaction (3) will be reduced.

For the activation energy values, it may be noted that the values of $E_2 - E_1$ for reaction (2) increases in the order of Li_2SiO_3, Li_4SiO_4 and SiO_2. This indicates that the formation of ODCs accompanied with the formation of peroxy linkages is much dependent on the material structures. In fact, the highest value is observed for SiO_2 in which the strongest linkage structure is expected. On the other hand, the values of $E_3 - E_1$ for the reverse reaction of reaction (1) are rather small and not so dependent on the materials. It is considered that the reverse reaction is promoted by the diffusing O_i, and that the similar values reflect the similarities of the O_i diffusion in these materials. In the case of the values of $E_4 - E_1$, it is also considered that the non-radiative transition of $Li_{2n}SiO^*_{2n+2}$ is related with the decomposition of peroxy linkages of which the activation energy is relatively high.

4. Conclusions

In order to know the production behavior of irradiation defects in the ternary lithium ceramics of Li_2SiO_3 and Li_4SiO_4, the transient behavior of luminescence intensities for temperature changes was studied as well as the temperature dependence of the luminescence intensity. The results of Li_2SiO_3 and Li_4SiO_4 were found to differ little from those of Li_2O and of the other ternary ceramics, and the production mechanism of irradiation defects was suggested in which ODCs were formed together with oxygen interstitials and peroxy linkages.

By taking the suggested production mechanism, the temperature dependence of the luminescence intensity was analyzed and the kinetic parameter values of the pre-exponential terms and activation energies were determined for the involved reactions. The obtained results were compared for different projectile ions and interpreted by considering different effects of linear energy transfer on the involved reactions. For further details of the production mechanism, investigation is suggested on the defect species themselves such as ODCs.

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