



Production behavior of irradiation defects in ternary lithium ceramics under ion beam irradiation

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Abstract

For the performance assessment of solid breeder materials for a fusion reactor, the production behavior of irradiation defects in some candidate materials of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 were studied by an in situ luminescence measurement technique under ion beam irradiation. The transient behavior of the luminescence intensity on temperature changes was measured in kinetic aspects of the involved reactions, and the production mechanisms and kinetics of the irradiation defects in these lithium ceramics were determined. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

In a fusion reactor of the solid blanket system, tritium breeding lithium ceramics are attacked by high energy neutrons and energetic particles from nuclear reactions, and severe irradiation damage may be expected. The irradiation behavior of lithium ceramics is thus important for the performance assessment of blanket systems for fusion reactors. 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 about the mechanism of the above effects [1,2].

For a clearer understanding of such effects, we have studied the production behavior of irradiation defects in Li_2O [3,4], LiAlO_2 [5], Li_2SiO_3 and Li_4SiO_4 [6,7] by an in situ luminescence measurement technique under ion beam irradiation. In Li_2O and LiAlO_2 , 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. Similarly, the irradiation defects of the E' center ($\equiv\text{Si}^\bullet$), the non-bridging oxygen hole center ($\equiv\text{Si}-\text{O}^\bullet$) and the peroxy radical ($\equiv\text{Si}-\text{O}-\text{O}^\bullet$) are produced in Li_2SiO_3 and

Li_4SiO_4 . These defects are considered to play an important role in the tritium behavior [8,9].

As for ternary lithium ceramics, some preliminary results of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 have been reported in our previous study [10]. In this case, multiple luminescence bands have been observed in the in situ luminescence measurement of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 under H^+ and He^+ ion beam irradiations. Also, an interesting temperature dependence of the luminescence intensity has been observed; the luminescence intensity under He^+ ion irradiation rises at the temperatures around 700 K while it decreases rather monotonically with increasing temperature under H^+ irradiation. In the temperature range whereby the luminescence intensity rises under He^+ irradiation, the luminescence bands of the wavelength shorter than 340 nm are observed more clearly in the spectra. From these findings, it has been suggested that the production mechanism of irradiation defects in these materials is rather similar to that in Li_2O .

The present study is an extension of our previous studies and deals with kinetic aspects of the production behavior of irradiation defects in the ternary lithium ceramics of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 . The transient behavior of luminescence intensities for temperature changes have been measured and analyzed to confirm the production mechanism. The obtained results are analyzed to determine the values of kinetic parameters of the involved reactions.

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2. Experimental

The lithium ceramics of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 were prepared by solid-state reactions. Powders of TiO_2 , ZrO_2 or SnO_2 of reagent grade from Nacalai Tesque, Inc. 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. Pellet-type samples of 10 mm in diameter and about 1 mm in thickness were sintered at 1423 K for 8 h. A He^+ or H^+ 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 monochromators, Ritsu MC-20N, and counted with photo-multipliers, 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. Observed transient phenomena

As already reported [6], multiple luminescence bands have been observed in the in situ luminescence measurement of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 under H^+ and He^+ ion beam irradiations. Although the lumines-

cence spectra were decomposed into a number of luminescence bands, most of these seemed to exhibit similar temperature dependences with one another in each material, and rather similar origins were suggested for these luminescence bands. Thus the present measurements of the transient behavior of luminescence intensities for temperature changes have been performed tentatively at the wavelength of 320 and 380 nm which are commonly observed in these ceramics.

Fig. 1 shows a typical result obtained with Li_2TiO_3 . For a temperature increase, the luminescence intensity first increases, thereafter it decreases and settles down to an equilibrium value. The observed phenomena seem to be similar to those for Li_2O in which the phenomena have been called the excess luminescence [3], but a certain difference is found between both cases. In the case of Li_2O , the excess luminescence was observed to depend on the irradiation time before the temperature change and to increase with the increasing irradiation time. Also, it was found that an intensity of the excess luminescence saturates at some equilibrium value which is roughly proportional to the second power of the beam current. The observed phenomena thus suggested that secondary reactions of irradiation defects are involved in the reaction mechanism. In the case of Li_2TiO_3 , on the other hand, such a dependence is hard to observe. As shown in Fig. 2, the excess luminescence is little dependent on the irradiation time except for the very early stage of irradiation. This means that the observed rise of the luminescence is not dependent on the irradiation

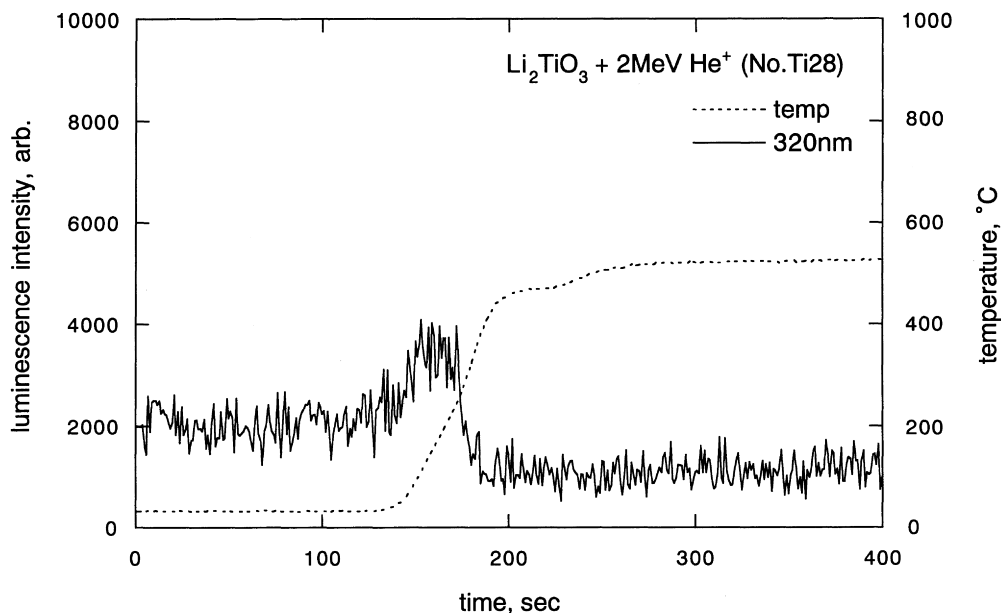


Fig. 1. Temperature-transient behavior of luminescence intensity at 320 nm for Li_2TiO_3 irradiated with 2 MeV He^+ ions of 8 nA. Irradiation time before a temperature increase is 600 s.

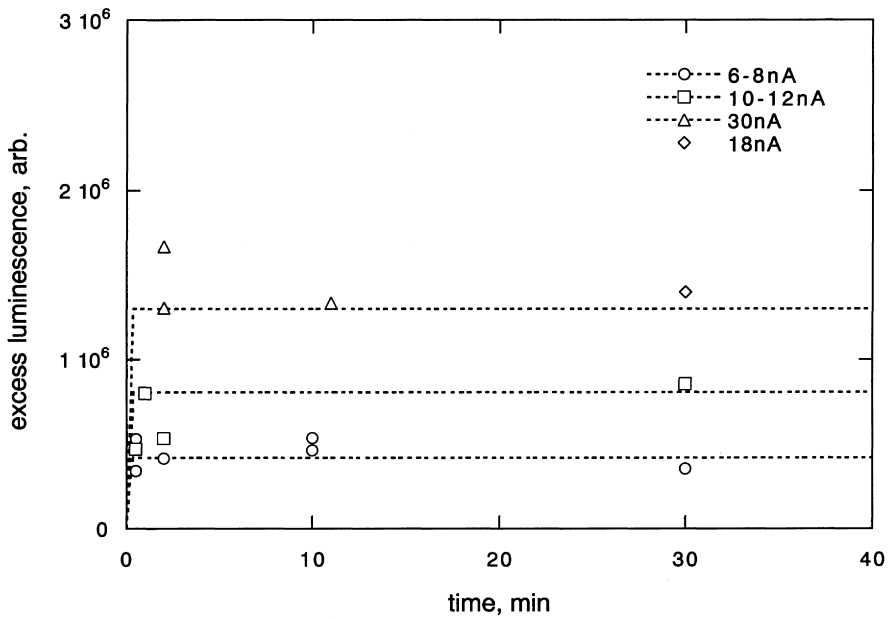
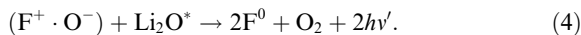
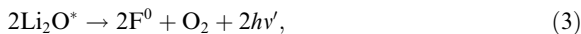


Fig. 2. Dependence of excess luminescence on irradiation time for Li_2TiO_3 irradiated with 2 MeV He^+ ions.

history and the equilibrium condition is attained rapidly for the involved reactions. Similar conclusions have also been obtained for Li_2ZrO_3 and Li_2SnO_3 .

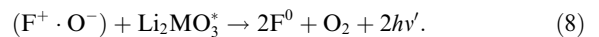
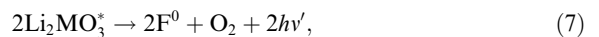
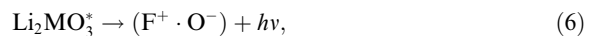
3.2. Production mechanism of irradiation defects

The production mechanism of irradiation defects in Li_2O [3,4], LiAlO_2 [5], Li_2SiO_3 and Li_4SiO_4 [6,7] have been studied in our previous work. In the case of Li_2O , the luminescence associated with the formation of F^+ centers is observed at low temperatures while that of F^0 centers is observed at high temperatures, and the following reaction scheme has been suggested for the production mechanism of F^+ and F^0 centers:



Reaction (1) represents the production of excited Li_2O (Li_2O^*) by ion beam irradiation. F^+ centers are considered to be associated with an O^- interstitial under Coulomb interaction as $(\text{F}^+ \cdot \text{O}^-)$ and to be produced by the first-order reaction (2). The second-order reactions (3) and (4) for the formation of F^0 centers require some thermal activation, and will take place at high temperatures. This is the reason why the luminescence of F^0 centers is observed especially at high temperatures.

By analogy of the reaction scheme for Li_2O , a similar production mechanism of irradiation defects in Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 has been given in our previous study [6], as



Following this reaction mechanism, two types of luminescence bands are considered; one is the luminescence associated with the formation of F^+ centers and the other with that of F^0 centers. The observed luminescence bands are thus classified into the two types. By considering the contribution of reactions (7) and (8), such temperature dependences in which the luminescence intensity under He^+ ion irradiation rises at the higher temperatures, around 700 K, have been explained.

In the present measurement, however, it has been shown that the transient behavior of the luminescence is little dependent on the irradiation history and the equilibrium condition is attained rapidly. This may suggest a little participation of reaction (8) in Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 , although the reaction scheme will be similar to that of Li_2O . In Li_2MO_3 , $(\text{F}^+ \cdot \text{O}^-)$ may be less stable and hardly accumulated.

3.3. 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 obtained results in the present study, some attempts are made here with the reported data on the temperature dependences of the luminescence intensity [10].

By assuming the above mentioned two types of irradiation defects, the observed luminescence intensity I is expressed as:

$$I = I_1 + I_2 = k_1[\text{Li}_2\text{MO}_3^*] + k_2[\text{Li}_2\text{MO}_3^*]^2, \quad (9)$$

where I_1 and I_2 are the luminescence intensities and k_1 and k_2 the rate constants of reactions (6) and (7), respectively. The life-time of Li_2MO_3^* is assumed to be very short and a steady-state approximation is applied to Li_2MO_3^* :

$$d[\text{Li}_2\text{MO}_3^*]/dt$$

$$= g' - k_1[\text{Li}_2\text{MO}_3^*] - k_2[\text{Li}_2\text{MO}_3^*]^2 - \sum_{i=3}^n k_i[\text{Li}_2\text{MO}_3^*] = 0, \quad (10)$$

where g' is the apparent generation rate of Li_2MO_3^* by reaction (5) and k_i ($i \geq 3$) the rate constants of the reverse reaction of reaction (5) and of some other non-radiative transition of Li_2MO_3^* . In order to calculate the luminescence intensity, the steady-state concentration of Li_2MO_3^* is obtained from Eq. (10) and substituted into Eq. (9).

In the present analysis, the reported data for the temperature dependence of the luminescence intensity have been fitted by Eqs. (9) and (10). The rate constants have been assumed to be of the Arrhenius type and hence the pre-exponential term A_i and activation energy term E_i have been determined. For a proper convergence, the number of the parameters to be fitted were reduced. By considering that the energy needed for the production of Li_2MO_3^* and its reactions are essentially the same in each lithium ceramic, the generation rate per unit deposited energy and the activation energy terms were assumed to be the same in each lithium ceramics irrespective of the different projectile ions, H^+ or He^+ . On the other hand, the pre-exponential terms were treated not to be the same for different projectile ions since different specific ionizations and hence different concentrations of Li_2MO_3^* in the ion tracks were expected to affect those values. As shown in Figs. 3–5, the agreements are satisfactorily good in all examined cases, and the values of obtained optimum parameters are summarized in Table 1.

Reaction (7) is the second-order type in the ion tracks, and some differences may be found due to the different projectile ions. As shown in Table 1, it may be noticed that, although the A_1/g' for re-

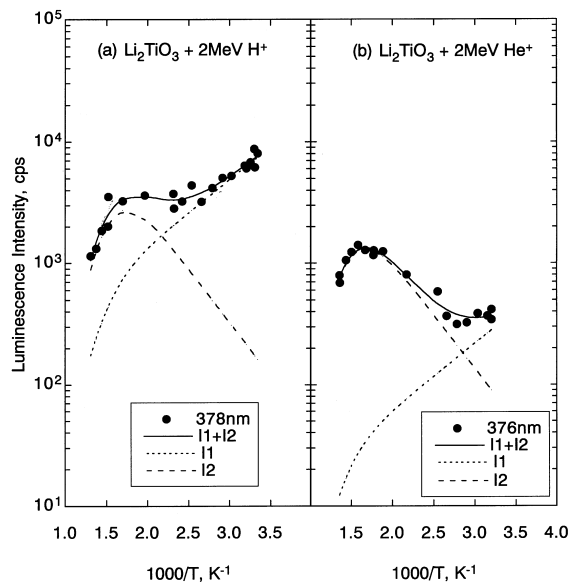


Fig. 3. Arrhenius plots of luminescence intensity of Li_2TiO_3 under (a) H^+ and (b) He^+ irradiation. The ordinate represents luminescence intensity corrected for beam current (1–30 nA). Marks are experimental [10] and curves represents the least-squares fits of the data by Eqs. (9) and (10).

action (6) is not so dependent on the projectile ions as expected for the first-order reaction, the A_2 value for reaction (7) is strongly dependent on the projectile ions. Also, the ratios of the A_2 values between He^+ and H^+ are found to be different in different materials and to increase in the order of Li_2TiO_3 : Li_2ZrO_3 :

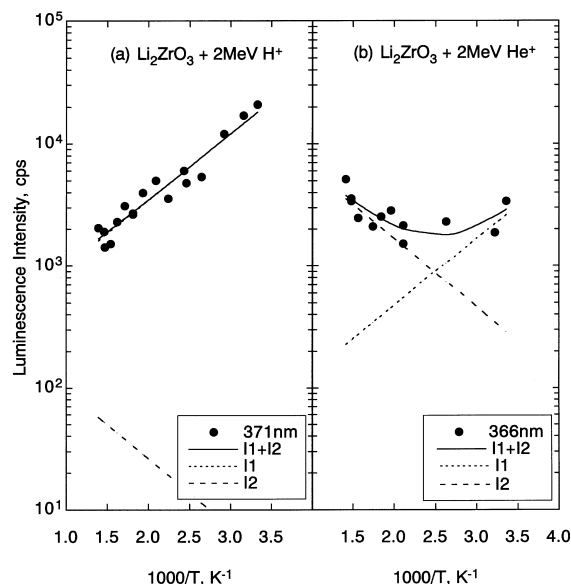


Fig. 4. Arrhenius plots of luminescence intensity of Li_2ZrO_3 under (a) H^+ and (b) He^+ irradiation. See also Fig. 3 captions.

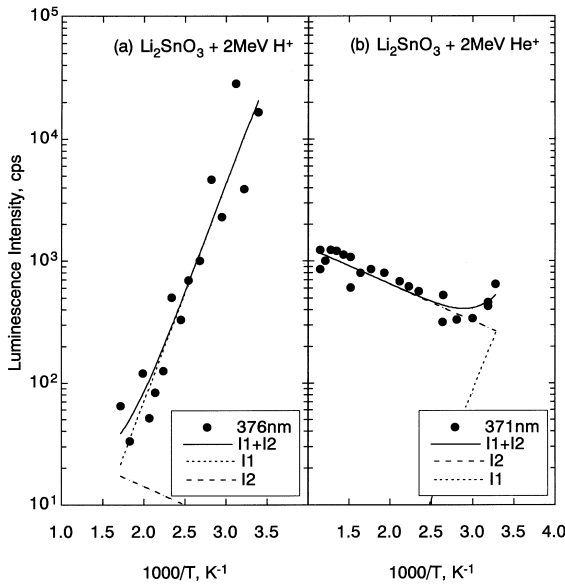


Fig. 5. Arrhenius plots of luminescence intensity of Li_2SnO_3 under (a) H^+ and (b) He^+ irradiation. See also Fig. 3 captions.

$\text{Li}_2\text{SnO}_3 = 1.0:1.7:3.9$. The observed trend can be interpreted by considering the characteristics of the local reactions in the ion tracks. Specific ionization and hence the local concentration of Li_2MO_3^* will increase with the increasing atomic number of the projectile ions and target materials. Then the A_2 values which reflect the differences in the local concentrations of Li_2MO_3^* will increase more effectively in the order of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 under He^+ ion irradiation than under H^+ ion irradiation. Consequently, the ratio of the A_2 values for He^+ and H^+ ions will increase in the same order as observed.

4. Conclusions

(1) In order to know the production behavior of irradiation defects in the ternary lithium ceramics of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 , the transient behavior of luminescence intensities for temperature changes was measured. A little dependence of the luminescence intensities on the irradiation time was observed and the equilibrium was found to be attained rapidly for the involved reactions.

(2) Comparing the results of Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 with those of Li_2O , it was found that the production mechanism of irradiation defects in these materials is similar to that in Li_2O . However, it was found that the contribution of such secondary reactions as the production of the F^0 centers in Li_2TiO_3 , Li_2ZrO_3 and Li_2SnO_3 is smaller than in Li_2O .

Table 1
Values of optimum parameters obtained from the analysis of in situ luminescence measurement data

Ceramics	Projectile ion	$k_1/g' = A_1 \exp(-E_1/RT)$		$k_2/g' = A_2 \exp(-E_2/RT)$		$k_3/g' = A_3 \exp(-E_3/RT)$		$k_4/g' = A_4 \exp(-E_4/RT)$		g' (s^{-1})
		A_1 (-)	E_1 (kJ/mol)	A_2 (-)	E_2 (kJ/mol)	A_3 (-)	E_3 (kJ/mol)	A_4 (-)	E_4 (kJ/mol)	
Li_2TiO_3	H^+	1.3×10^{-4}	-0.3	5.6×10^{-1}	37.3	3.2×10^0	10.2	9.8×10^3	55.7	2.6×10^6
	He^+	1.8×10^{-4}	(-0.3) ^a	2.1×10^2	(37.3) ^a	9.7×10^1	(10.2) ^a	2.0×10^5	(55.7) ^a	$(2.6 \times 10^6)^a$
Li_2ZrO_3	H^+	7.3×10^{-6}	0.4	1.7×10^{-6}	32.3	1.9×10^{-1}	10.8	-	-	7.4×10^6
	He^+	3.2×10^{-6}	(0.4) ^a	1.1×10^{-3}	(32.3) ^a	6.0×10^{-1}	(10.8) ^a	-	-	$(7.4 \times 10^6)^a$
Li_2SnO_3	H^+	4.3×10^{-9}	15.7	5.9×10^{-5}	105.6	4.4×10^0	49.9	-	-	1.8×10^7
	He^+	4.9×10^{-10}	(15.7) ^a	8.6×10^{-2}	(105.6) ^a	2.5×10^1	(49.9) ^a	-	-	$(1.8 \times 10^7)^a$

^a Assumed to be the same for both H^+ and He^+ ion irradiation of each ceramic. See text.

(3) By taking the suggested production mechanism, the temperature dependence of the luminescence intensity was analyzed and the values of kinetic parameters such as the pre-exponential terms and activation energies were determined for the involved reactions. The obtained results were interpreted by considering the characteristics of the reactions in the ion tracks.

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