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High energy heavy ion induced structural disorder in Li_2TiO_3

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Abstract

Li_2TiO_3 ceramics have been irradiated with xenon (Xe) ions in the energy range of 18–160 MeV at ambient temperature. The effect of ion irradiation on the order in the atomic arrangement of Li_2TiO_3 crystal was examined by X-ray diffraction (XRD) and Raman spectroscopy. The results show that the atomic arrangement in Li_2TiO_3 is strongly disordered by the high energy Xe ion irradiation. The destruction of long-range order due to the irradiation was confirmed from the reductions in XRD intensities of the (0 0 2) supercell reflection. The destruction of short-range order was confirmed from the reductions in the Raman intensities and disappearances of Raman bands with fluence. The disordering is more efficient with the increase in the electronic stopping power than with fluence or accumulated electronic energy deposition. These disorders due to the irradiation are discussed in relation to irradiation parameters such as electronic stopping power, accumulated electronic energy deposition and fluence.

1. Introduction

Lithium metatitanate (Li_2TiO_3) is regarded as one of the most suitable candidates for the solid tritium breeder material of D–T fusion reactors [1]. It is known that, in an operating fusion reactor, the radiation damage will be produced in Li_2TiO_3 by fast neutrons, energetic tritons (2.7 MeV) and helium ions (2.1 MeV) generated by $^6Li(n,\alpha)^3H$ reaction. The damage caused by ionising radiation may result in microstructural changes [2] and hence may have an impact on the tritium release behavior and on thermal and mechanical properties of Li_2TiO_3. Thus, the study of microstructural changes and irradiation defects in Li_2TiO_3 is quite important for the evaluation of its irradiation performance. In spite of this, little is yet known about the mechanism of the above effects for Li_2TiO_3 [3,4]. Many are known about those for other oxides [2,5,6]. Recent studies [2,5,6] have shown that ionization due to electronic stopping power can play an important role in radiation damage in ceramics. So, it is necessary to examine the effects of ionization on ceramic fusion materials such as solid breeder materials, insulators, etc.

Recently, the simultaneous exposure of Li_2TiO_3 to H^+, He^+ and O^{2+} ions in the temperature range of 343–873 K at a fluence of 1.0×10^{21} m^{-2} has been

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reported to cause the appearance of TiO_2 (anatase) phase in its surface layer [7]. In addition, the crystal form of fused Li_2TiO_3 has been confirmed to be disordered at ambient temperature by high energy ions (160 MeV Xe, 80 MeV O) [8]. The disordering due to ion irradiation is closely related with the threshold value of electronic stopping power of incident ions. In order to obtain further information on disorder caused in Li_2TiO_3 by irradiation, Li_2TiO_3 was exposed to Xe ions with energies of 18–160 MeV and examined by X-ray diffraction and Raman spectroscopy measurements.

2. Experimental procedure

The Li_2TiO_3 was produced from 99% pure powder purchased from CERAC, Inc. The powder was cold pressed at 300 MPa into cylinders subsequently sintered at 1223 K for 6 h in an Ar atmosphere. The resulting Li_2TiO_3 was approximately 78% of theoretical density (3.43 g/cm^3 [1]). The X-ray diffraction (XRD) pattern and Raman spectrum taken for the Li_2TiO_3 ceramics crushed into fine fragments confirm that the products are of single phase with a monoclinic structure. The specimens, machined from the cylinders in the form of disks with a diameter of 10 mm and a thickness of ~1.0 mm, were used for irradiation.

The irradiations with high energy Xe ions of 18–160 MeV were performed for the Li_2TiO_3 ceramics at ambient temperature using the Tandem Accelerator of JAEA. The fluences were in the range of 2.4×10^{16} to 4.9×10^{17} m^{-2}. The SRIM 2000 code [9] was used to estimate the damage parameters such as the electronic (S_e) and nuclear (S_n) stopping powers and accumulated electronic energy deposition (defined as S_e multiplied by fluence). Characteristics of ion irradiations for Li_2TiO_3 are summarized in Table 1.

The irradiated samples were examined by XRD and Raman spectroscopy. The XRD patterns were obtained using a Cu Kα radiation for the samples before and after irradiation. During XRD measurements, samples were masked with a gold foil of 10 μm in thickness having a square hole sized 8 by 5 mm in order to avoid any diffraction from the unirradiated portion. The intensities of diffraction peaks from samples were normalized to that of a specified diffraction peak from the gold foil. Raman spectra were measured for samples before and after irradiation at ambient temperature with JASCO NR 1100 Raman spectrometer operated at 100 mW using the 488 nm line of Ar laser as the excitation source.

3. Results and discussion

3.1. X-ray diffraction

Li_2TiO_3 has the monoclinic structure in which the cations occupy octahedral sites in a cubic close-packed oxide ion array. The ordered structure has different cation ordering sequences associated with the different stoichiometries. The nature of the disordering transformation caused by the quenching with rapid cooling has been shown by X-ray diffraction [10]. In disordered material, XRD peaks corresponding to the cation-ordered superstructure was not present. The disappearance of superstructure XRD peaks shows that there is no long-range order in the cation arrangement.

The highest peak corresponding to the (002) supercell reflection has been observed at $2\theta = 18.6°$ in the XRD patterns measured for Li_2TiO_3 samples [10]. The reductions in the (002) supercell peak intensities are observed for the present samples irradiated with the 18–160 MeV Xe ions. The irradiation causes the reduction in XRD peak intensity in a manner similar to the case of quenching by rapid

Table 1
Characteristics of Xe ion irradiations for Li_2TiO_3

Ion	Xe			
E (MeV)	18	39	80	160
R_p (μm)	5.9	8.7	13.0	18.0
Fluence (ions/m^2)	2.4×10^{16}, 2.4×10^{17}, 4.9×10^{17}	2.4×10^{17}	2.4×10^{17}	2.4×10^{17}
D (GGy)	0.01, 0.08, 0.17	0.14	0.19	0.24
S_e (keV/nm)	5.7	9.7	13.1	16.7
S_n (keV/nm)	0.12	0.07	0.04	0.02

E: energy of ions, R_p: mean projected range, D: accumulated radiation dose, S_e: electronic stopping power at near surface, S_n: nuclear stopping power at near surface. R_p, S_e and S_n are estimated with the SRIM 2000 code [9].

cooling. The peaks are observed to be nonsymmetric for both small and large angles, along with the reductions in the peak intensities due to the irradiations. The reductions in the (0 0 2) peak intensities mean that the destruction of long-range order of the cation arrangement in superstructure of Li_2TiO_3 is caused by the irradiation. The nonsymmetric peaks indicate that the expansion and contraction of the (0 0 2) supercell were caused by the irradiation. Specifically, the irradiation causes disorder of the arrangement of Li and Ti cations in the superstructure of Li_2TiO_3, as the quenching does the partial site mixing between Li and Ti sites. The disorder due to the irradiation is accompanied by the expansion and contraction of the (0 0 2) supercell. Also, the Li and Ti cations in Li_2TiO_3 become disordered at above 1213 °C [10]. Thus, the impact of irradiation on the arrangement of Li and Ti cations around the trajectories of incident ions is considered to correspond to that of the quenching from temperature above 1213 °C.

Fig. 1 shows the changes of (0 0 2) peak intensities for the accumulated electronic energy deposition $\langle D\rangle$. The symbol $\langle\,\rangle$ of $\langle M\rangle$ stands for the average of M as the damage parameter for the damaged region estimated with the SRIM 2000 code. The peak intensities are reduced with the increase in the $\langle D\rangle$ value. In the case of the 18 MeV Xe ion irradiations with the $\langle S_e\rangle$ of 2.8 keV/nm, the peak intensity is drastically reduced with the increase in the $\langle D\rangle$ value for the fluence from 2.4×10^{16} to $2.4\times10^{17}\ m^{-2}$. The increase in the $\langle D\rangle$ value for the fluence from 2.4×10^{17} to $4.9\times10^{17}\ m^{-2}$ does not cause more reduction in the peak intensities. On the other hand, the increase in $\langle S_e\rangle$ value, which is realized by the increase in the acceleration energy, causes further reduction of the peak intensity. The (0 0 2) peak is completely disappeared by the 160 MeV Xe ion irradiation at fluence of $2.4\times10^{17}\ m^{-2}$, which gives the $\langle D\rangle$ value of 0.29 GGy for the damaged region.

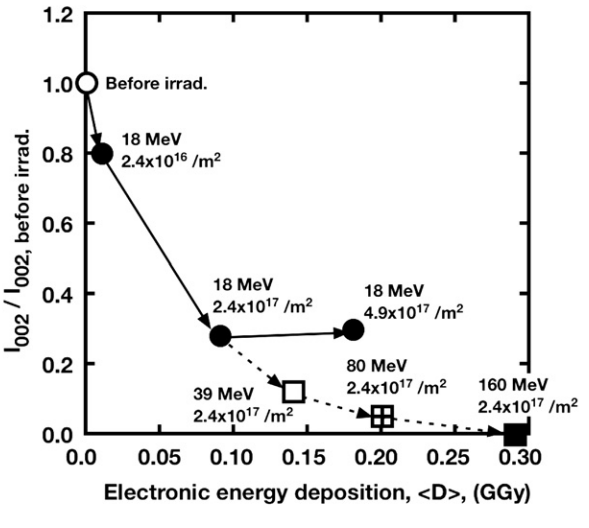

Fig. 1. Changes of X-ray diffraction peak intensities due to irradiation, plotted against accumulated electronic energy deposition, $\langle D\rangle$, which is averaged for the damage regions estimated with the SRIM 2000 code [9]. Numerical values in figure are energies of ions and fluences.

No change of the (0 0 2) XRD peak intensity due to the 18 MeV Xe ion irradiation is observed when the fluence was increased from 2.4×10^{17} to $4.9\times10^{17}\ m^{-2}$. The independence of XRD intensity with fluence increase is considered to be due to the XRD signals being originated from the non-damaged region in depth of specimen. The XRD signal intensities observed are mainly expressed by the function of both depth from surface of sample and 2θ. The intensity of incident X-rays is reduced with the increase in depth where the X-rays are diffracted. The projected range of the 18 MeV Xe ions was calculated for the Li_2TiO_3 with the SRIM 2000 code to be 5.9 μm. The intensity of incident X-ray is estimated to be reduced to about 12% by the diffraction at the depth of 5.9 μm. Thus, the (0 0 2) XRD intensities from the samples, which are irradiated by the 18 MeV Xe ions, contain the signal intensity from both damaged regions and non-damaged ones. This independent intensity is reduced by the increase in the acceleration energy of Xe ions. These results show that the increase in the acceleration energy makes the damaged region thicker. Therefore, the long-range order is considered to be fully disappeared in the damaged region by the 18 MeV Xe ion irradiations at the fluence of $2.4\times10^{17}\ m^{-2}$. Note that the thickness of the disorder region becomes larger only by the increase in the acceleration energy.

The disorder region caused by the ion irradiation has been observed for magnetic oxides to be formed along the track of the high energy ion [11] and also numerous other oxides and other ceramics [5,6]. The track morphology depends on the value of the energy loss for the high energy ions. The disorder region formed along the ion track is represented as a cylinder along ion trajectory [11–14]. The cross section of disorder region α has been given by $I_\sigma/I_0 = e^{-\alpha\sigma}$, $I_{\sigma,0}$ being XRD peak intensities at fluence σ, 0. The α may be expressed as $\alpha = \pi r_A^2$, where r_A is the ultimate stable radius of the disorder region. This relationship has been extensively discussed in previous studies [13,14].

For the Li_2TiO_3 samples irradiated by 18 MeV Xe ions, the radius r_A of disorder region formed along the ion track is roughly estimated to be about 2.1 nm from the XRD experimental values using the above expression. The amount of track area, if calculated as $\pi r_A^2 \sigma$, exceeds the damaged area, and the excessive area is assumed to be overlapped. For the fluence of 2.4×10^{16} m^{-2}, the ratio of excessive area to amount is estimated about 14%. For the fluences of 2.4×10^{17} and 4.9×10^{17} m^{-2}, the ratios are about 70% and 85%, respectively. In cases of 70% and 85% ratios, the damaged region is considered to be completely disordered by the irradiation because the reduction in XRD peak intensities are not observed with increase of the fluence from 2.4×10^{17} to 4.9×10^{17} m^{-2}. For the 39–160 MeV Xe ion irradiated Li_2TiO_3 samples, the XRD experimental data are insufficient to estimate the radius of track.

3.2. Raman spectroscopy

The influence of ion irradiation on the Raman spectra is similar to that observed for the XRD patterns. Raman spectra of the samples before and after irradiation are shown in Fig. 2. The vibrational spectra of lithium titanate oxides have been studied using the results of group-theoretical analyses [15,16]. The information on the short-range order in Li_2TiO_3 can be seen from Raman spectra before irradiation. In lithium titanate, the frequencies in the 700–550 cm^{-1} region are known to be assigned to Ti—O stretching in TiO_6 octahedra. In oxides, where lithium is octahedrally coordinated by oxygen, the frequencies of the Li—O stretching are known to lie within the 250–400 cm^{-1} region. When the lithium coordination is tetrahedral, the frequencies lie in the 400–550 cm^{-1} region. In the Li_2TiO_3 structure, the lithium occupies both octahedral and tetrahedral positions.

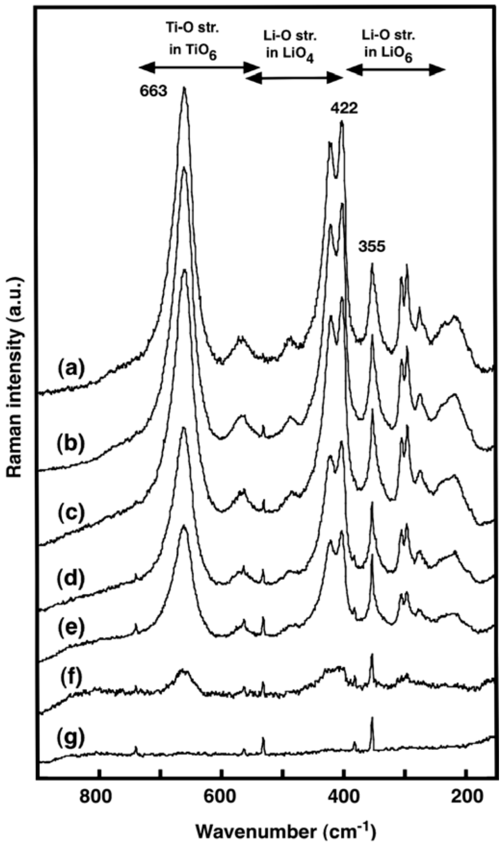

Fig. 2. Changes in Raman spectra of Li_2TiO_3 irradiated with high energy Xe ions. The values of S_e, S_n (keV/nm), fluence (m^{-2}) and D (GGy) for each spectrum labeled with (a)–(g) are as follows: S_e: (a) 0, (b,c,d) 5.7, (e) 9.7, (f) 13.1, (g) 16.7; S_n: (a) 0, (b,c,d) 0.12, (e) 0.07, (f) 0.04, (g) 0.02; fluence: (a) before irradiation, (b) 2.4×10^{16}, (c) 2.4×10^{17}, (d) 4.9×10^{17}, (e,f,g) 2.4×10^{17}; D: (a) 0, (b) 0.01, (c) 0.08, (d) 0.17, (e) 0.14, (f) 0.19, (g) 0.24. The values of S_e, S_n and D are estimated at surface of sample by the SRIM 2000 code [9].

The profiles of Raman spectra are observed in Fig. 2 to be changed by the irradiation. The changes of profiles and peak intensities are remarkable with the increase in the value of S_e, but not the value of S_n. Raman peaks of the samples, irradiated by 18 MeV Xe ions with a S_e value of 5.7 keV/nm at surface, are slightly reduced when the fluence increases from 2.4×10^{16} to 4.9×10^{17} m^{-2} (Fig. 2(b)–(d)). The peak heights for the 663 cm^{-1} peak of Ti—O bond vibration and the 422 cm^{-1} peak of Li—O bond vibration relative to the 355 cm^{-1} peak for Li—O are plotted in Fig. 3 against electronic energy deposition at the surface, D. They are 3.4 and 2.8 before irradiation, and are reduced to 2.2 and 1.8, respectively, with the increase in 18 MeV Xe ion fluence from 2.4×10^{16} to 4.9×10^{17} m^{-2}. The height ratios are reduced to 1.65 and 1.35 with the increase in the S_e value from 5.7 to 9.7 keV/nm (Xe ion energy increased from 18 to 39 MeV) with the fluence being the same value of 2.4×10^{17} m^{-2}. Almost no Raman peaks can be observed for the samples irradiated with larger S_e value, such as 13.1 and 16.7 keV/nm for the irradiation to 2.4×10^{17} m^{-2}. Note that the white circles and black squares with (c), (e), (f) and (g) in Fig. 3 are data observed for the samples irradiated with different acceleration energy to same fluence,

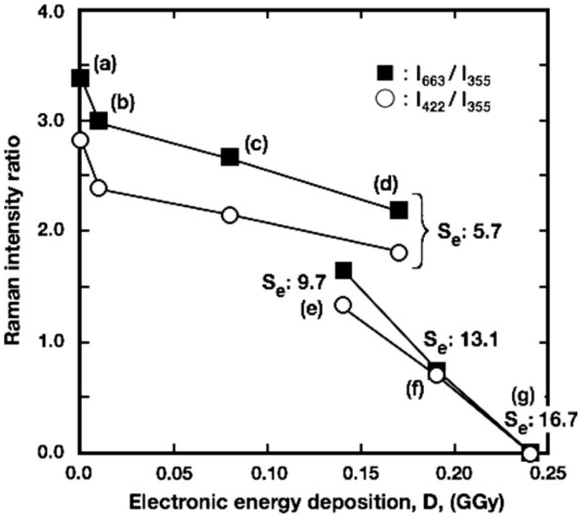

Fig. 3. Changes in Raman intensity ratio of Li_2TiO_3 irradiated with high energy Xe ions, plotted against accumulated electronic energy deposition, *D*, at surface. Labels (a)–(g) given to each ratio correspond to those used in Fig. 2. Acceleration energies (MeV) and fluences (m^{-2}) are as follows: (a) before irradiation, (b) 18, 2.4×10^{16}, (c) 18, 2.4×10^{17}, (d) 18, 4.9×10^{17}, (e) 39, 2.4×10^{17}, (f) 80, 2.4×10^{17}, (g) 160, 2.4×10^{17}. The values of S_e (keV/nm) are also shown.

i.e. 2.4×10^{17} m^{-2}. Especially, the peak of Ti—O vibration in TiO_6 octahedra completely disappeared. A negligible peak observed around 740 cm^{-1} corresponds to the Ti—O vibration in TiO_4 tetrahedra [15]. On the other hand, the weak peaks of Li—O vibrations remain. The formation of new phases and decompositions, such as TiO_2, are not found from results of Raman analyses.

Such reduction and disappearance of Raman peaks due to the irradiation indicate that the ordering of structural units in Li_2TiO_3, such as TiO_6, LiO_6 and LiO_4 units, is lost. This destruction of short-range order due to the irradiation is significantly related to the S_e value, but is less dependent on the fluence and *D* value. The main factor causing the destruction of short-range order in Li_2TiO_3 due to the high energy Xe ion irradiation is considered to be the S_e of incident ions.

From comparison of the changes in XRD patterns and Raman spectra due to the irradiation of Li_2TiO_3, it is shown that the disorder can be characterized by the value of S_e. The small value of S_e causes nearly complete destruction of long-range order due to the irradiation, i.e. disorder of lattice structure, while the short-range ordering such as TiO_6, LiO_6 and LiO_4 units are only partially destroyed (<50% change in Raman peak ratio). As the value of S_e at surface of sample increases from 5.7 to 16.7 keV/nm, significant S_e dependence for all values from 5.7 to 16.7 keV/nm are actually observed in the Raman spectrum. The changes mean that the destruction of short-range order is caused by destruction of the structural units due to the breaking of chemical bonds surrounding the ion track. Some loss of short-range order also occurs at 5.7 keV/nm and the loss of both short-range order and long-range order occurs more rapidly with increasing S_e between 5.7 and 16.7 keV/nm. These results indicate that the character of disorder caused by the high energy ion irradiation is closely related to the value of S_e.

4. Conclusions

The results of XRD and Raman spectroscopic analyses indicate that the structural disorder of Li_2TiO_3 irradiated with 18–160 MeV Xe ions is characterized by the value of the S_e.

The examination of Li_2TiO_3 exposed to 160 MeV Xe ions by Raman spectroscopy provides evidence of the destruction of structural units in Li_2TiO_3. In contrast, the structural units of Li_2TiO_3 exposed to 18 and 39 MeV Xe ions were not appreciably destroyed though the destruction of long-range order was caused by the Xe ion irradiation. Hence, the extent of disordering resulting in the destruction of structural units in Li_2TiO_3, that is, the destruction of short-range order, is considered to be significantly associated with the S_e of incident ions of more than 10 keV/nm. Thus, the main factor causing the disorder by ion irradiation is considered to be the S_e of the incident ions.

In this study, the ionization energies due to S_e are suggested to cause the disordering in Li_2TiO_3. The disordering is considered to impact on tritium release process. It is necessary to systematically study about role of S_e on radiation damage of solid breeder material, especially under the conditions close to those of the blanket exploitation.

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