

Oxygen defects created in CeO₂ irradiated with 200 MeV Au ions

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Abstract

CeO₂ films were irradiated with 200 MeV Au ions in order to investigate the damages created by electronic energy deposition. In the Raman spectra of the ion-irradiated films, a broad band appears at the higher frequency side of the F_{2g} peak of CeO₂. The band intensity increases as ion fluence increases. Furthermore, the F_{2g} peak becomes asymmetric with a low frequency tail. In order to understand the origin of these spectral changes, an unirradiated CeO₂ film was annealed in vacuum at 1000°C. By comparing the results for the irradiation and for the annealing, it is concluded that the broad band obtained for irradiated samples contains the peak observed for the annealed sample. The F_{2g} peak becomes asymmetric with a low frequency tail by the irradiation as well as the annealing. Therefore, the above-mentioned changes in the Raman spectra caused by 200 MeV Au irradiation is closely related to the creation of oxygen vacancies.

PACS codes: 61.82.Ms, 61.80.Jh

Keywords: High energy ion irradiation, Electronic energy deposition, Radiation damage, Oxygen vacancy, Raman spectroscopy, thermal annealing

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1. Introduction

Ceramic fuel pellets of UO_2 are widely used in light water reactors (LWRs). During irradiation, radiation defects are mainly caused by fission fragments accumulated in the matrix. Ion irradiation has been used extensively in order to simulate the radiation damage process under the conditions of fission.

In case of oxide, it is known that heavy damage such as amorphization occurs as a result of high density electronic energy deposition caused by high energy ion irradiation, for example, in SiO_2 [1], and YBaCuO [2]. While UO_2 shows a relatively high radiation-resistance against high-energy heavy ion irradiation compared to the oxides mentioned above. No amorphization is reported for UO_2 irradiated with high-energy heavy ions, but so-called ion tracks are created [3].

CeO_2 can be regarded as a simulation-material for investigating radiation damage in UO_2 . There are close similarities between CeO_2 and UO_2 in terms of melting temperatures (CeO_2 : ~ 2700 °C, UO_2 : 2865 ± 15 °C [5]), lattice constants (CeO_2 : 5.406743 Å [6], UO_2 : 5.47176 Å [7]) and their crystallographic structures (fluorite structure). As same as UO_2 , CeO_2 is not amorphised, but ion tracks are created by high-energy ion irradiation [4].

X-ray diffractions of CeO_2 irradiated with 200 MeV Au ions were already reported [8]. The work shows that the lattice is expanded by the irradiation. However, the origin of the expansion is not identified. One of the reasons of the expansion is creation of oxygen defects [6].

In this work, in order to investigate the damage process created by electronic energy deposition, a Raman spectroscopic analysis is performed for the CeO_2 films irradiated with 200 MeV Au ions. In order to investigate the effect of oxygen vacancy, vacuum annealing experiment for an unirradiated CeO_2 film is also performed. The Raman spectra obtained after the irradiation and those obtained after the annealing are compared.

2. Experimental procedure

CeO_2 films with thickness of 0.3 μm were deposited on sapphire R plane by magnetron sputtering. 200 MeV Au^{+13} irradiation was performed at room temperature at the tandem accelerator of Japan Atomic Energy Agency, Tokai Research and Development Center (JAEA-Tokai). According to SRIM 2006 [9], electronic stopping power is 32.0 MeV/ μm , while nuclear stopping power is 0.320 MeV/ μm under the present condition. Ion fluences were in the range from 2×10^{11} to 8×10^{12} ions/ cm^2 . After the irradiation, damages were studied by Raman scattering. Raman measurements were conducted by using a confocal Raman microscope (Nanofinder, Tokyo instruments) with an Ar^+ laser of 488nm wavelength and 0.3mW laser power.

In order to create oxygen vacancies, an unirradiated CeO₂ film was annealed in vacuum ($\sim 10^{-6}$ Torr) for 1 hour at 1000°C. Before and after the thermal annealing, Raman spectra were measured in the air at room temperature. The Raman measurement was performed just after the annealing (within 1 hour).

3. Results and discussion

The Raman spectra obtained for unirradiated CeO₂ sample exhibit a peak at 464 cm⁻¹ ascribed to Raman active mode of CeO₂ (F_{2g} peak). The Raman spectra obtained for the irradiated samples show F_{2g} peak and background signal. The background was subtracted from the spectra for the irradiated samples. Figure 1 (a) shows the spectra after subtraction of their background. The peak at 464 cm⁻¹ is ascribed to Raman active mode of CeO₂ (F_{2g} peak). Fluorite structure metal dioxides have only a single allowed Raman mode, which has F_{2g} symmetry and can be viewed as a symmetric breathing mode of the O atoms around each cation. In the figure, the spectra are normalized by the intensity of the F_{2g} peak. The small peak at 432cm⁻¹ is due to sapphire substrate. The positions of the objective lens were adjusted to give maximum F_{2g} peak intensities, respectively.

The spectra for the irradiated samples show a new broad band appeared at the higher frequency side of the F_{2g} peak. The band range is from about 500 cm⁻¹ to 650cm⁻¹. The intensity of the band increases as the fluence increases. The spectra also show that the F_{2g} peak becomes asymmetric with a low frequency tail after the irradiation.

Figure 1 (b) shows the normalized Raman spectra obtained before and after annealing. Since these spectra show very small background, the background is not subtracted. The figure show that a new peak appears at higher frequency side of F_{2g} peak after the annealing. This peak has the maximum intensity at 538cm⁻¹ and that has broad width extending to high frequency side of about 700cm⁻¹. The spectra also show that the F_{2g} peak becomes asymmetric with a low frequency tail.

The oxygen vacancies in CeO₂ has been previously reported for doping experiment. In the previous literature, the Raman spectra of CeO₂ doped with RE (RE = La, Pr, Nd, Eu, Gd, and Tb) were reported [10]. According to the spectra of the study, a new feature appears near 570cm⁻¹ by the doping. Furthermore, F_{2g} mode for La-, Nd-, Eu-, and Gd-doped samples becomes asymmetric with a low-frequency tail as amount of dopant increases. A mathematical model based on Green's function was used to attribute these results to oxygen vacancies. These results of doping experiment and model calculation pointed out that a new broad peak and asymmetric F_{2g} peak are the characteristics of CeO_{2-y} with oxygen vacancies.

A new broad peak and asymmetric F_{2g} peak are also found in annealed sample as mentioned above. Spectral change in the annealed sample can be also ascribed to oxygen vacancy.

In the spectra obtained for the irradiated samples, a new band appeared, and it contains the peak observed for annealed sample. The asymmetric F_{2g} peak observed for the irradiated samples is also related to oxygen vacancy. Those features indicate that oxygen vacancy is created in the irradiated samples.

Here we have to discuss whether the contribution of nuclear collision to oxygen vacancy is sufficiently small. The electronic energy deposition contributes to creation of nanometer-size ion track [4], while nuclear collision contributes to only 1700ppm oxygen vacancies at 1×10^{13} ions/cm² according to the SRIM-2003 calculation [9]. Therefore, most of the oxygen vacancies probed by Raman spectroscopy is due to electronic energy deposition.

There are some differences between the spectral change caused by the irradiation and that caused by the annealing. The band observed for the irradiated samples contains not only the peak ascribed to oxygen vacancy but also another broad contribution. Furthermore, the growing background obtained after the irradiation is not obtained by the annealing. The F_{2g} peak observed for the irradiated sample is much broader than that observed for the annealed sample. These differences suggest that the crystallinity of CeO₂ is disordered by the high energy ion irradiation, which agrees with the earlier studies [4, 8].

4. Conclusion

In order to investigate the effect of electronic energy deposition, Raman analyses are conducted for the CeO₂ films irradiated with 200 MeV Au at room temperature. The Raman spectra after the irradiation show a new broad band at higher frequency side of F_{2g} peak. Furthermore, the Raman active F_{2g} peak becomes asymmetric with a low frequency tail. In order to study the effect of oxygen vacancy on the Raman spectrum, an unirradiated CeO₂ film was annealed in vacuum at 1000°C. The Raman spectrum after the annealing shows a new peak at higher frequency side of the F_{2g} peak and the F_{2g} peak becomes asymmetric with a low frequency tail as well as the irradiation. The above results indicate that the spectral changes caused by the irradiation are closely related to oxygen vacancy.

Acknowledgements

The authors are grateful to the technical staff of the accelerator facilities at JAEA-Tokai for their great help.

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Figure captions

Fig.1 Raman spectra obtained from (a) irradiated samples and (b) annealed sample. Each of these spectra is normalized by the intensity of F_{2g} main peak.

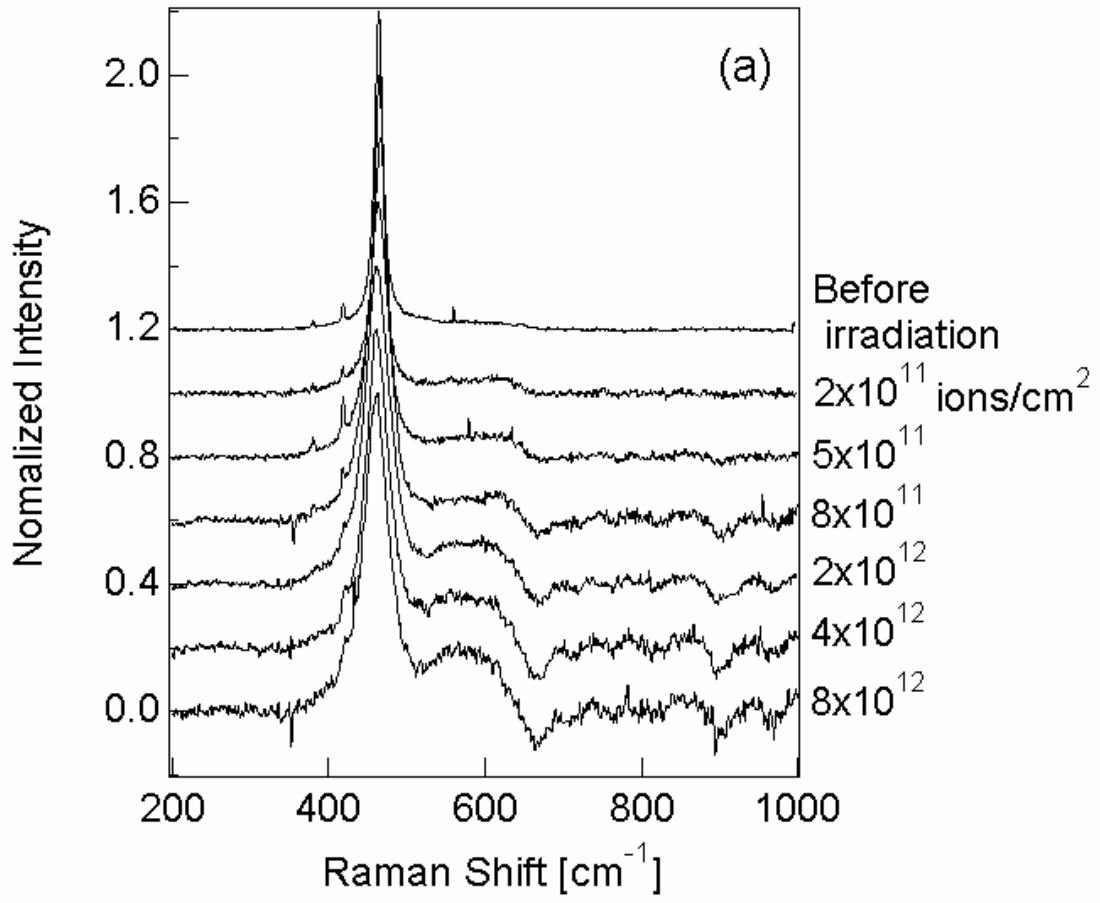


Fig. 1 (a) K. Ohhara et al.

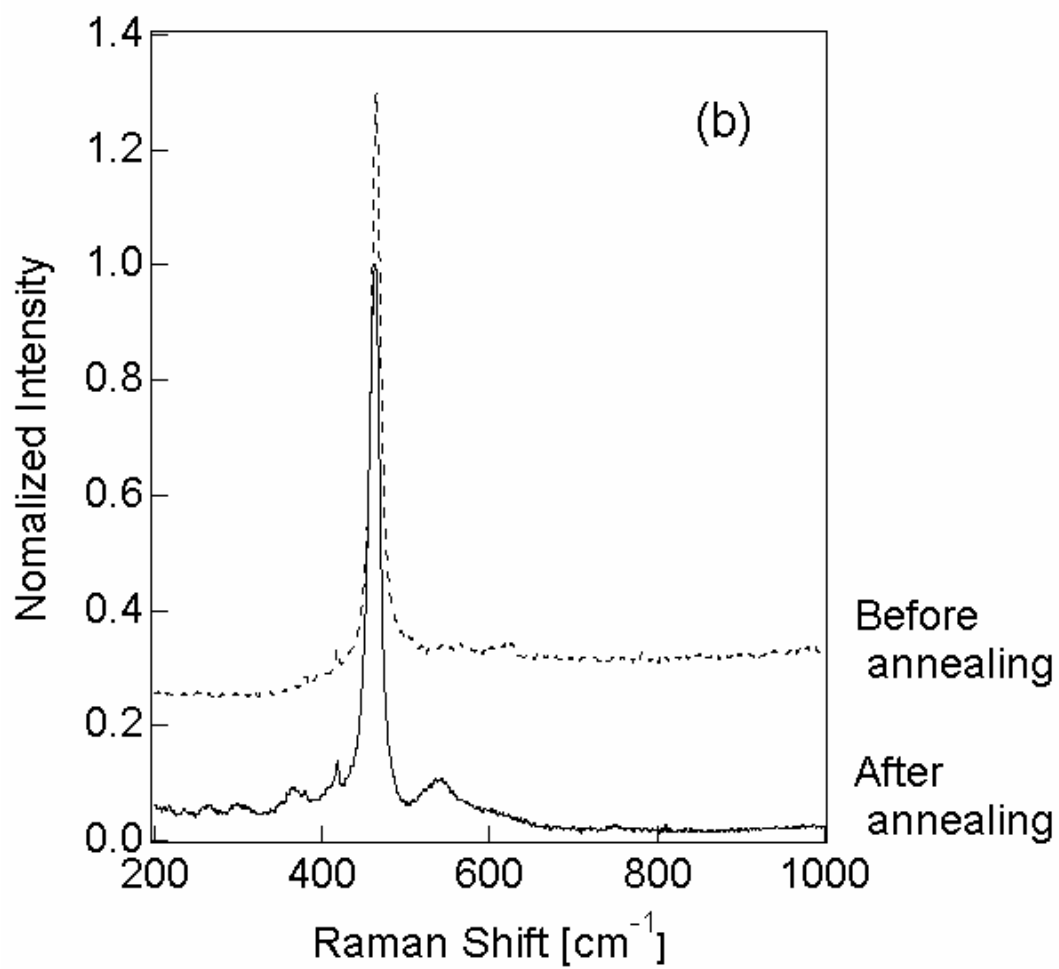


Fig. 1 (b) K. Ohhara et al.