Study on the Point Defects Production and Microstructure Change in Ceria Based Oxides

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論 文 名：Study on the Point Defects Production and Microstructure Change in Ceria Based Oxides
(セリア系酸化物の点欠陥形成と微細構造変化に関する研究)

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論 文 内 容 の 要 旨

Ceramic oxide with fluorite structure, such as ceria (CeO_2), has been proposed as a surrogate of nuclear fuels (e.g. UO_2, PuO_2) and transmutation targets because of the excellent radiation resistance. Ceria has a redox effect between two charge states of cerium ions with localized *f* electrons, which induces oxygen vacancies (V_O) to compensate for charge neutrality. Gadolinia (Gd_2O_3) exhibits a bixbyite structure, and it has been doped in UO_2 fuel as a burnable poison due to the large absorption cross-section of thermal neutrons. Gd_2O_3-doped CeO_2 as expressed by $Ce_{1-x}Gd_xO_{2-x/2}$ also produces V_O since the Gd^{3+} substitutes into the Ce^{4+} site. The oxygen deficiency in $Ce_{1-x}Gd_xO_{2-x/2}$ is mainly controlled by the dopant concentration.

Moreover, V_O can be generated by elastic collisions with high-energy electrons by receiving energy above the threshold displacement energy of oxygen atoms. The V_O is a key factor to determine radiation tolerance since it enhances the recombination of interstitials and vacancies. The kinetic behavior of point defects in ceramics is known to depend on their charge states. However, there was only limited research on it since the *in-situ* techniques are needed to gain the production and charge state of point defects in ceramics during irradiation.

In this dissertation, radiation damage in $Ce_{1-x}Gd_xO_{2-x/2}$ was investigated for a wide range of Gd dopant concentrations ($0 \le x \le 0.5$). For this purpose, a unique facility of a high voltage electron microscope (HVEM) interfaced with cathodoluminescence (CL) facility at The Ultramicroscopy Research Center of Kyushu University was utilized to examine the production and charge state of point defects *in-situ* under high-energy electron irradiation. Further, microstructure change induced by heavy ion irradiation was studied comprehensively against dopant concentration by x-ray diffraction (XRD) analysis, micro-Raman spectroscopy, and transmission electron microscopy (TEM) to understand the role of oxygen vacancy on the microstructure stability. This dissertation consists of seven chapters.

Chapter 1 described the introduction and research goal of this study. At the end of this chapter, the structure of the dissertation was outlined.

Chapter 2 reviewed the theoretical and experimental background on structure in CeO_2 and $Ce_{1-x}Gd_xO_{2-x/2}$. Displacement damage, energy loss, diffraction analysis for structure evaluation, and CL emission mechanism were described in this chapter.

Chapter 3 explained the experimental methodology for the sample preparation, and the techniques of XRD, Raman spectroscopy, and TEM. Details for the synthesis of $Ce_{1-x}Gd_xO_{2-x/2}$ samples and ion irradiation conditions were described. *In-situ* CL measurement conditions were also described together with the data acquisition procedures.

Chapter 4 described point defect production under in-beam conditions in pure single crystal and polycrystalline ceria using the *in-situ* HVEM-CL technique. The CL spectra were obtained with 400 ~ 1250 keV electrons, and they were fitted into three CL bands. One band was assigned to be the F^+ center which is induced by electron-nuclear elastic collisions, and the other two bands were originated from charge-compensative Ce^{3+} ions caused by V_O formation. Localized atomic configurations between Ce^{3+} ions and charged V_O were suggested according to the CL spectra. The dependence of CL spectra against electron energy and irradiation temperature were also explained by taking the cross-sections of defect production and electronic excitation.

Chapter 5 discussed microstructure and radiation response in $Ce_{1-x}Gd_xO_{2-x/2}$ for a wide range of Gd_2O_3 concentrations ($0 \leq x \leq 0.5$). Microstructure characterization was carried out comprehensively by XRD, micro-Raman spectroscopy, and TEM. The formation of bixbyite structure with V_O ordering was observed for $x \geq 0.2$, associated with the saturation of lattice parameter and micro-strain relaxation. Those microstructure changes with values of x were found to influence the microstructure change induced by 200 MeV Xe ions. Ion track density and size were found to be depressed for samples with $x \geq 0.2$, and this was discussed with the ordering of V_O which attributes to the recovery process of radiation-induced defects.

Chapter 6 described the application of the *in-situ* HVEM-CL technique to $Ce_{1-x}Gd_xO_{2-x/2}$ samples. The CL bands for Ce^{3+}-V_O, Ce^{3+}, and F^+ center were observed from $Ce_{1-x}Gd_xO_{2-x/2}$ as same as pure ceria. The electronic configurations and energy dependence of CL spectra in $Ce_{1-x}Gd_xO_{2-x/2}$ were compared with those of pure ceria. Photon energy shifts and quenching of CL emission were observed in $Ce_{1-x}Gd_xO_{2-x/2}$, and the change was discussed with the generation of V_O induced by Gd_2O_3 doping, and the change of electrical configuration around Ce^{3+} ions and V_O. The band gap energy level of defects in $Ce_{1-x}Gd_xO_{2-x/2}$ was suggested in this chapter.

In chapter 7, all the experimental and simulation works done in the wake of this study are summarized as conclusions together with possible directions for future research.