§43. Study on Mechanism of Luminescence Property Change in Irradiated Functional Materials

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In the development of fusion blanket systems, usage of various oxide, carbide, nitride, hydride functional materials have been proposed for electrical insulation, suppression of tritium fuel permeation, suppression of corrosion, radiation shielding, etc. The uv-vis-nir emission spectra in these materials excited by charged particle beam or photon have been used as a measure for characterization of their properties. However, the effect of crystallinity on the emission spectra and its mechanism are not understood well enough. In previous study, cathodoluminescence (CL) measurement is performed on several materials to examine the understanding of CL mechanism. From the results, it has been found that the intensity in 640-700 nm had a correlation with crystallinity in Er_2O_3 coatings [1]. On the other hand, the discussion on mechanism in CL of each materials is still begun to be studied, and will be proceeded with using examples from the earlier studies of each materials in the other research area. The analyses of electronic states by the DV-Xα molecular orbital calculation method and Gaussian 09 have also been implemented in this study, since each properties of the materials may depend on their electronic states. For promoting the discussion on the relationship between the results of electron energy level structure and emission mechanism, and its application for crystallinity estimation, Y_2O_3, whose CL spectra had been measured and compared in the samples that have different crystallinity, is selected to study.

Local electronic structures around oxygen ion vacancy in Y_2O_3 are simulated by the DV-Xα molecular method. The cluster models used are constructed on the basis of the crystal structure of Y_2O_3 at room temperature. In order to take account of the Madelung potential between ions, point charges are arranged around the cluster. Fig. 1 shows the changes in the energy level structures near the band gap with introduction of oxygen ion vacancy into Y_2O_3. Here, the occupied molecular orbitals are indicated by solid lines and the unoccupied molecular orbitals are indicated by dotted lines. The respective cluster models used in the calculation are summarized below each energy level structures. Model (a) and model (c) are pure Y_2O_3, and consist of 55 ions and 106 ions, respectively. In (b) and (d), one oxygen ion vacancy is introduced to (a) and (c), respectively. The HOMO level for Y_2O_3 (model (a)) is set to be zero and used as a reference of the energy. The energy band of pure Y_2O_3 is mainly composed of the O-2p valence band and the Y-4d conduction band. As shown in Fig. 1(a) and (c), the band gap between them is about 7 eV. This values is close to the experimental results, 5.6-5.8eV, but it is overestimated. In comparison with (a) and (c), it is found that enlargement of cluster size results in slight

improvement in this overestimation. As is evident from results in (b) and (d), the electronic structure is modified largely, mainly around conduction band, by the introduction of oxygen ion vacancy into the Y_2O_3.

Theoretical Raman spectrum is calculated by Guassian 09. In this calculation, cluster model is used to avoid the high calculation load as in using periodic boundary condition. Fig. 2 shows (a) experimental [2] and (b) calculated Raman spectra. Although the calculated spectrum have some similar peaks of experimental results, this simulation requires further improvement.
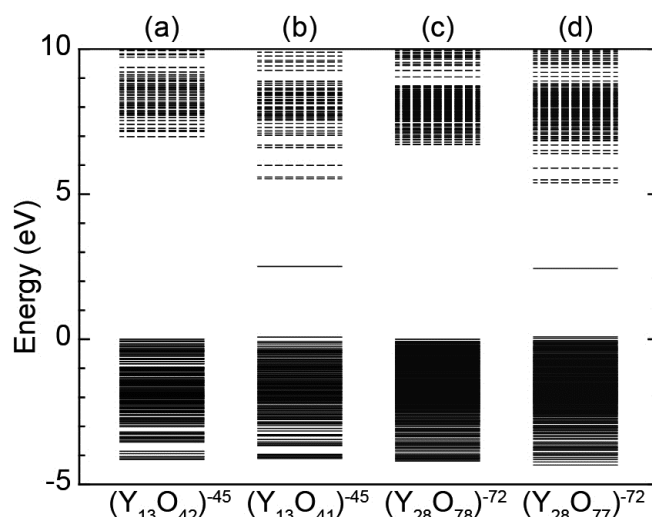

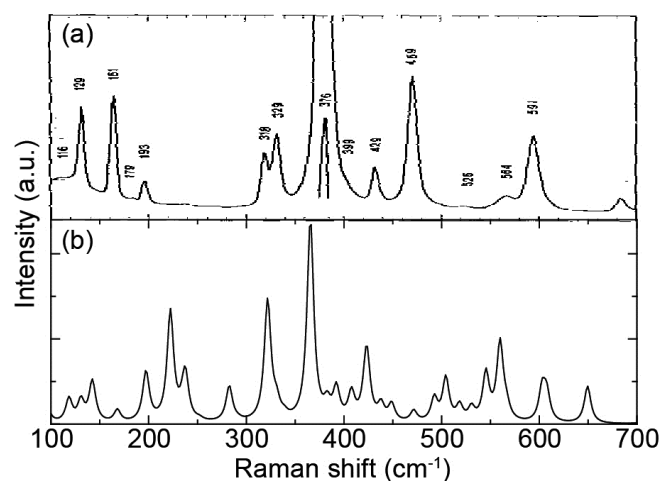Fig. 1 Changes in the energy level structures near the band gap with the introduction of oxygen ion vacancy into Y_2O_3.

Fig. 2 Raman spectra of Y_2O_3. ((a) experiment [2], (b) calculation)

[1] Tanaka, T., et al., Journal of Nuclear Materials 417 (2011) 794-797.
[2] Repelin, Y., et al., Journal of Solid State Chemistry 118 (1995) 163-169.