AMTC Letters
Vol. 1 (2008)

Local electronic and atomic structures of Ce^{3+}-containing materials by TEM-EELS and first principles calculations

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A Ce 4*f* electron in Ce^{3+}-containing materials exhibits specific properties such as luminescence and fast oxygen-absorption / desorption. In their EEL spectra, the Ce M_4/M_5 relative peak intensity ratios are known as a measure of oxidation states of Ce, although fine structures in the M_4 and M_5 edge are difficult to be understood by electronic structure calculations within the one-electron approximation. The spectral structure of anionic edge (e.g. O-*K* and F-*K* ELNES) is additional useful information to understand the electronic and atomic structures of the materials because it reflects generally the unoccupied electronic density of states (DOS) that could be estimated by the calculations. This study investigates the electronic/atomic structures of (1) typical materials containing Ce^{3+} (CeF_3 and Ce_2O_3) and (2) ceria-zirconia ordered phases which are used as a co-catalyst for automobile applications. Their theoretical calculations were made based on the density functional theory (DFT) and DFT+U.

(1) CeF_3 and Ce_2O_3

F-*K* spectra of a CeF_3 powder sample were measured by TEM-EELS at 160 kV accelerating voltage. To minimize the effects of the electron irradiation damages, the acquisition time was set as 2 s for an illuminated area. Since we did not succeed in acquiring O-*K* spectra of the original phase because of severe oxidation of the Ce_2O_3 powder particles during TEM sample preparation, Fig. 1-b shows the experimental O-*K* spectrum reported by Garvie *et al.*[1].

Figure 1 compares between the experimental and theoretical *K*-shell spectra. In both compounds, the spectral shape of the GGA+U result is more consistent with that of the experimental. As indicated in the figure, the energy width of the main peaks of the oxide spectrum is larger than that of the fluoride. This energy region reflects the width of Ce *d* bands. From the viewpoint of atomic orbital interaction, it is found that 1) the energy width is formed by atomic orbital interaction among atoms within an approximately 7 Å area (100 atoms), 2) the difference in the energy width between the compounds is due to the difference in the antibonding interaction between Ce 5*d* and anion 2*p*; CeF_3 in which Ce is more isotropically coordinated by anions and the interaction is homogeneous over different directions of the 5*d* orbitals, has the narrower Ce 5*d* energy band. These findings suggest that the bandwidths of Ce *f-d* luminescence among different Ce^{3+} containing materials could be clarified systematically according to the local atomic arrangements around Ce.

(2) Ceria-zirconia ordered phases

Figure 2 shows the O-*K* spectra of $Ce_2Zr_2O_7$, which is the reduced phase in the ceria-zirconia system ($Ce_2Zr_2O_X$ X=7, 7.5 and 8). In this phase, oxygen vacancies are ordered and accordingly O ions are displaced from the ideal positions based on the fluorite structure. As shown in Fig.2-d, O ions are displaced toward Zr and away from Ce. In order to investigate the electronic structure differences caused by the oxygen displacements, theoretical spectra (Fig.2-b) of the ideal and displaced models are compared with the experimental (Fig. 2-a). The spectral profile of the displaced model is more consistent with that of the experimental. The partial DOS (Fig. 2-c) indicated that the electronic structures ranging over about 10 eV from the Fermi level are significantly different between the models. The oxygen displacements split Zr(Ce) *d* DOS peaks in larger (smaller) energies, which suggests that the displaced model has stronger Zr-O bonds and nearly free Ce ions.

References

[1] L.A.J. Garvie et al., J. Phys. Chem. Solids, **60** (1999) 1943.
[2] S. Muto et al., J. Electron Microscopy **55** (2006) 225.

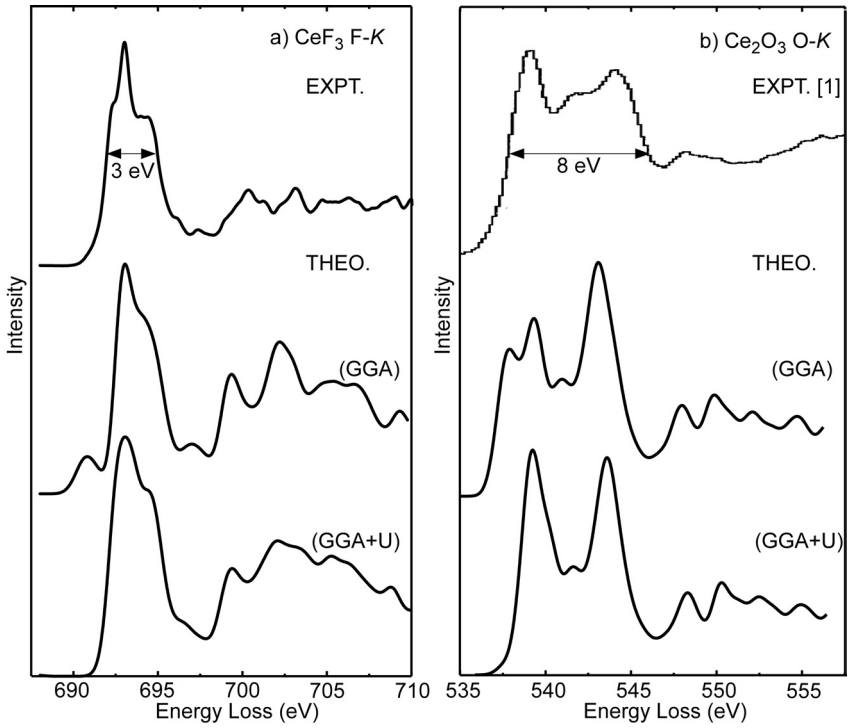

FIG. 1. Experimental and theoretical F-*K* (a) and O-*K* (b) spectra. The experimental F-*K* spectrum is restored by the procedure reported in ref. [2]. The spectra were aligned so that the main peaks are at the same energies.

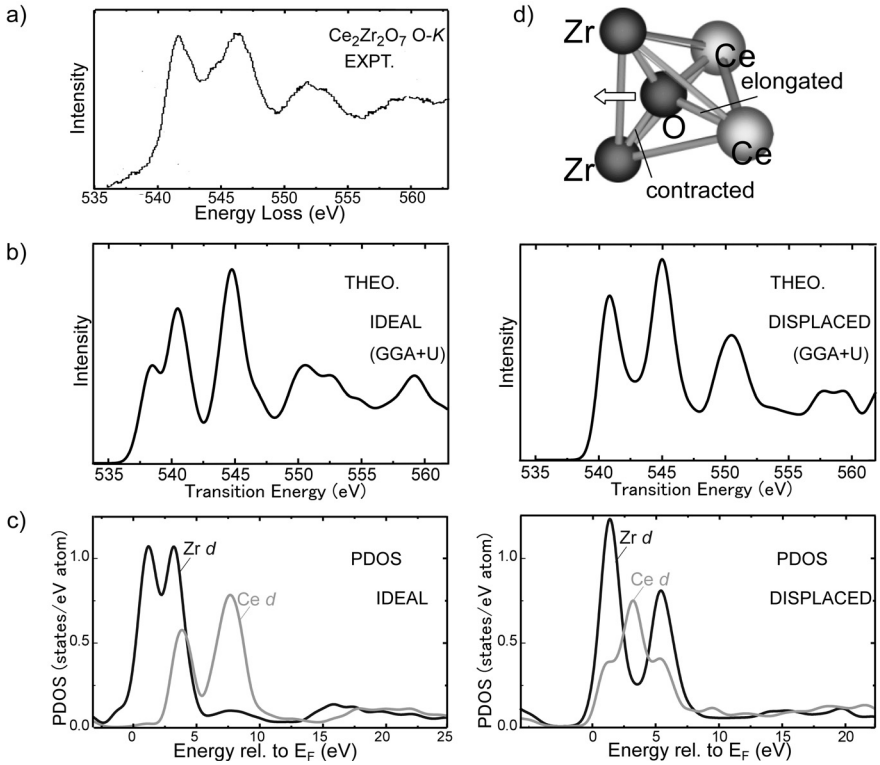

FIG. 2. Experimental (a) and theoretical (b) O-K spectra of $Ce_2Zr_2O_7$, corresponding partial density of states of the cations (c) and oxygen displacement in this compound (d).