

## Local structure of perovskite-type (A,Eu)Ta(O,N)<sub>3</sub> (A=Ca,La) oxynitrides

Shinichi KIKKAWA<sup>\*1</sup>, Yuji MASUBUCHI<sup>1</sup> and Akira Yoshiasa<sup>2</sup>

<sup>1</sup>Hokkaido Univ., Sapporo 060-8628, Japan

<sup>2</sup>Kumamoto Univ., Kumamoto 860-8555, Japan

### Introduction

Tantalate oxynitrides have been attracting potential applicability for nontoxic inorganic pigments and photocatalysts. Both pyrochlore and defect fluorite-type structures have been reported as high temperature phases of rare-earth tantalate oxynitrides [1]. R<sup>3+</sup>TaON<sub>2</sub> perovskite (R: rare-earth) has been assumed as their low temperature phase. Interesting dielectric property has been reported on B<sup>2+</sup>TaO<sub>2</sub>N (B: alkaline earth) perovskites [2]. Their phase relation and the ordering especially of anions in the perovskites should be clarified from the structural view points.

### Experimental

Calcium carbonate, europium oxide and tantalum pentachloride were dissolved in absolute ethanol with equimolar citric acid to the total amount of cations to prepare (Ca,Eu)Ta(O,N)<sub>3</sub> solid solution. They were heated on a hot plate under stirring to obtain viscous gel. It was heated at 350°C for 1hour and then nitrided in ammonia flow at 1000°C for 15hours. Lanthanum oxide was used instead of calcium carbonate in the preparation of (La,Eu)Ta(O,N)<sub>3</sub> solid solution.

### Results and discussion

Orthorhombic and cubic perovskite phases were obtained below and above  $x=0.4$ , respectively, in Ca<sub>1-x</sub>Eu<sub>x</sub>Ta(O,N)<sub>3</sub>. Their unit cell expanded well with  $x$ . LaTaON<sub>2</sub> perovskite has been reported to be monoclinic [3]. The present La<sub>1-y</sub>Eu<sub>y</sub>Ta(O,N)<sub>3</sub> was cubic and the lattice parameter slightly shrunk with  $y$ . The EuTa(O,N)<sub>3</sub> was cubic with  $a=0.40152\text{nm}$ . There was no characteristic change in absorption edges of Ca K, La and Ta LIII along with the chemical compositions of  $x$  and  $y$ . Eu LIII edge showed only the presence of Eu<sup>2+</sup> at the europium end of  $x=y=1$ . Trivalent Eu<sup>3+</sup> also appeared with their decrease in  $x$  and  $y$ . Their EXAFS region was Fourier transformed to obtain radial distribution around the x-ray absorbing atoms. There was no practical change in the first neighbor with the compositions of  $x$  and  $y$  around Ca, La and Ta. The first nearest neighbor around Eu expanded with the compositions  $x$  and  $y$  as shown in Figs.1 and 2. The second and the third nearest neighbors were also clearly observed on the EuTa(O,N)<sub>3</sub> corresponding to Eu-Eu and Eu-Ta, respectively.

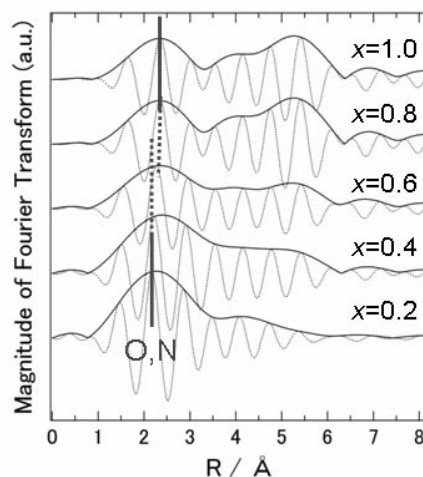


Fig. 1 Fourier transforms of Eu LIII-edge EXAFS for the Ca<sub>1-x</sub>Eu<sub>x</sub>Ta(O,N)<sub>3</sub> perovskite.

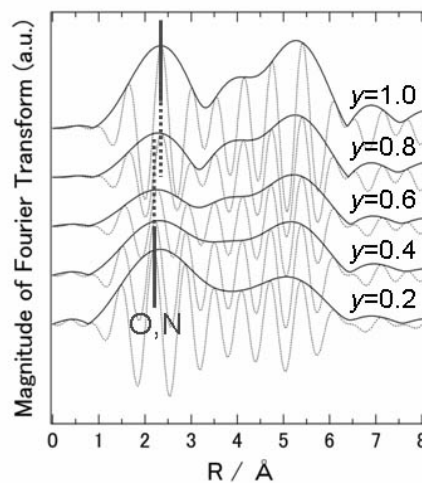


Fig. 2 Fourier transforms of Eu LIII-edge EXAFS for the La<sub>1-y</sub>Eu<sub>y</sub>Ta(O,N)<sub>3</sub> perovskite.

### References

- [1] P. Maillard, F. Tessier, E. Orhan, F. Chevire and R. Marchand, Chem. Mater., 17, 152-156 (2005).
- [2] Y. Kim, P. Woodward, K. Baba-Kishi and C. Tai, Chem. Mater., 16, 1267-1276 (2004).
- [3] E. Gunther, R. Hagenmayer and M. Jansen, Z. Anorg. Allg. Chem., 626, 1519-1525 (2000).

\*kikkawa@eng.hokudai.ac.jp