

Local structures of defective fluorite- and pyrochlore-type R-tantalate oxynitride (R= Nd, Y)

Shinichi KIKKAWA^{*1}, Takashi TAKEDA² and Akira Yoshiasa³

¹Hokkaido Univ., Sapporo 060-8628, Japan

²NIMS, Ibaraki 305-0044, Japan

³Kumamoto Univ., Kumamoto 860-8555, Japan

Introduction

Crystal structure of rare-earth tantalate oxynitride RTa(O,N) has been reported as pyrochlore for the larger rare-earths (R=Nd→Gd) and fluorite for the smaller rare-earths R=Ho, Er, Yb and Y [1]. In the present study, Y K-, Nd and Ta LIII-edge EXAFS were employed to investigate local structure around both rare-earth and tantalum atoms in the oxynitrides (R= Nd, Y).

Experimental

Rare-earth oxides dissolved in concentrated hydrochloric acid and tantalum oxalate solution were used as starting materials. Citric acid was added to their stoichiometric mixture in aqueous solution. The solution was polymerized under stirring at 150°C for 20 min and then heated at 250°C for 5 h to an expanded black solid residue. This solid was ground and calcined at 600°C in air. It was then nitrated at 800~900°C for 15 h in ammonia flow.

Results and discussion

XRD showed that YTa(O,N)₄ had a defect fluorite-type structure, while Nd₂Ta₂O₅N₂ had a pyrochlore structure [1]. Absorption edges of Nd LIII, Y K and Ta LIII were very similar for the present oxynitride samples prepared at 900°C and their respective references. Both neodymium and yttrium are trivalent and tantalum is pentavalent. Their EXAFS region was Fourier transformed to obtain radial distributions around the x-ray absorbing atoms. The refined distances in Nd₂O₃ reference agree well with the values reported from the structural analysis. There were two kinds of radial distribution for Nd-(O,N) at 0.18 nm and 0.26 nm in the present Nd₂Ta₂O₅N₂ as shown in Fig. 1. The Nd-O distances were refined as 0.226 nm and 0.263 nm by curve-fitting. Another distribution for Nd-Ta was 0.35 nm. These two kinds of oxygen and/or nitrogen around Nd in Nd₂Ta₂O₅N₂ suggest the structure is pyrochlore type. The radial distribution around yttrium was less clear in YTa(O,N)₄ than that around neodymium in Nd₂Ta₂O₅N₂. The first nearest distribution for Y-(O,N) appeared at 0.17 nm as a single peak as depicted in Fig. 2 and refined to be 0.241 nm. The second nearest distribution appeared at 0.32 nm for Y-(Y,Ta). These distances correspond to 0.23 nm and 0.37 nm in the ideal fluorite type structure. The low resolution of the Fourier transform may also suggest a distribution of Y-(O,N) bonding distances in the defect fluorite type crystal structure. Both Nd₂Ta₂O₅N₂ and YTa(O,N)₄ exhibited similar radial distribution spectra around tantalum. The tantalum atoms are coordinated

with six nitrogen/oxygen atoms in the present samples, Nd₂Ta₂O₅N₂ and YTa(O,N)₄, because the first nearest distributions are located at almost the same distances as the references. The details have been published [2].

References

- [1] P. Maillard, F. Tessier, E. Orhan, F. Chevire and R. Marchand, Chem. Mater., 17, 152-156 (2005).
- [2] S. Kikkawa, T. Takeda, A. Yoshiasa, P. Maillard and F. Tessier, Mater. Res. Bull., 43, 811-818 (2008).

*kikkawa@eng.hokudai.ac.jp

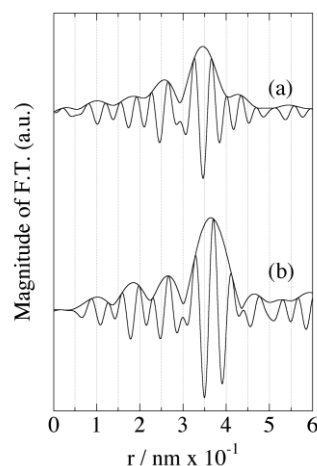


Fig. 1 Fourier transforms of Nd LIII-edge EXAFS for the (a) Nd₂Ta₂O₅N₂ sample and (b) Nd₂O₃ reference.

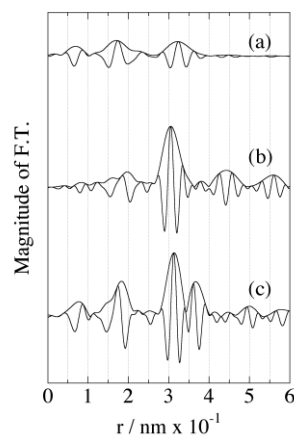


Fig. 2 Fourier transforms of Y K-edge EXAFS for the (a) YTa(O,N)₄ sample, (b) YN and (c) Y₂O₃ references.