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Local structures of cubic EuTa(O,N)$_3$ oxynitride substituents

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Introduction

Tantalum oxynitride perovskites ATaO$_2$N (A: alkali-earth and rare-earth elements) have attracted much attention due to their unusual dielectric properties [1]. BaTaO$_2$N and SrTaO$_2$N exhibit bulk permittivity (κ) as large as 3000 ~ 5000. The dielectric properties seem to be related to the crystal structure, as κ of orthorhombic CaTaO$_2$N is much smaller (≈ 30) than that of the Ba-analogue with cubic symmetry. For SrTaO$_2$N, on the other hand, the structure was refined based on either tetragonal [1,2] or cubic model [3]. It has not been well understood what material parameters are predominant for determining the crystal structure of tantalum oxynitride perovskites. To address this issue, we focused on EuTa(O,N)$_3$. This compound can be a structural reference for SrTaO$_2$N, since the ionic radius of Eu^{2+} is close to that of Sr^{2+}. In the present study, the structure and anionic composition of EuTa(O,N)$_3$ were investigated. A series of the Ca$_{1-x}$Eu$_x$Ta(O,N)$_3$ system was synthesized and characterized in order to clarify how the properties are influenced upon substituting Eu for Ca.

Experimental

Ca$_{1-x}$Eu$_x$Ta(O,N)$_3$ samples with x = 0, 0.2, 0.4, 0.6, 0.8, and 1.0 were synthesized by ammonia nitridation at 1000°C *via* a citrate precursor route, as described elsewhere [4]. Nitrided products were characterized by X-ray powder diffraction (XRD). The anionic composition was determined using an oxygen/nitrogen analyzer. X-ray absorption of Eu L$_{\mathrm{III}}$- and Ta L$_{\mathrm{III}}$-edges was measured in transmission mode at the beam line 9C in Photon Factory.

Results and discussion

XRD analysis indicated that all of the Ca$_{1-x}$Eu$_x$Ta(O,N)$_3$ products are of single phase. The products with $x < 0.4$ were apparently orthorhombic, while those with $x \geq 0.4$ crystallized in a cubic structure. The anionic composition was found to be essentially O$_2$N and independent of Eu content (x). Figure 1 shows Eu L$_{\mathrm{III}}$-edge XANES spectra of Ca$_{1-x}$Eu$_x$Ta(O,N)$_3$. The spectra consist of two peaks in all the Eu-containing products. Since the low-energy ($E \approx$ 6970 eV) and high-energy ($E \approx$ 6980 eV) peaks are similar to those for the EuCl$_2$ and Eu$_2$O$_3$ standards, the former and the latter are accordingly attributed to the $2p_{3/2} \rightarrow 5d$ transition of Eu^{2+} and Eu^{3+}, respectively. Therefore, europium ions are in mixed valent between +2 and +3. The Eu^{3+} peak is large in x = 0.2 because its ionic size is small enough to occupy the Ca^{2+} site, while its intensity systematically decreases with increasing x. In x = 1.0 (EuTaO$_2$N), europium is mainly divalent with a small amount of trivalent species.

The Eu^{2+}/Eu^{3+} coexistence is easily explained if the Eu-containing products are assumed to be slightly off-stoichiometric with N-rich compositions. The presence of excess nitride anions in EuTaO$_2$N was indeed reported previously [5]. Another possible explanation is that tantalum is also mixed-valent between Ta^{4+} and Ta^{5+} so as to compensate extra positive charges of europium. It was not possible to determine the Ta valence by means of XANES spectroscopy without ambiguity, because the positions of L$_{\mathrm{III}}$-edge are close to each other for Ta^{4+} and Ta^{5+}.

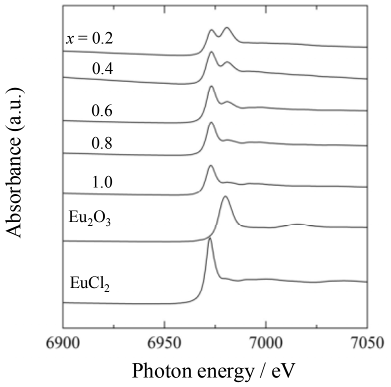

Fig. 1 Eu L$_{\mathrm{III}}$-edge XANES spectra of Ca$_{1-x}$Eu$_x$Ta(O,N)$_3$ with x = 0.2, 0.4, 0.6, 0.8, and 1.0. The reference spectra of Eu$_2$O$_3$ (Eu^{3+}) and EuCl$_2$ (Eu^{2+}) are also shown.

References

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