Reconstruction of oxynitrides is a new trend in developing new functional materials. Getting information about the local structure around the cation is crucial because the arrangement of the anions affects the cations and the displacement of cations can be related to their physical properties. To study the effects of mixed anions on the behavior of the cations in oxynitrides, we applied X-ray fluorescence holography on a CaTaO$_2$N thin film. Atomic images reconstructed from Ta L$_\alpha$ holograms clearly showed the atomic positions around Ta. By comparing the intensities of the Ta and Ca atomic images, we found that the fluctuations of the Ta atoms are larger than the Ca atoms.

**Keywords** X-ray fluorescence holography; Oxynitride; Perovskite; Local structure analysis

**I. INTRODUCTION**

A lot of functional materials used in commercial applications contain expensive elements [1, 2]. Researchers have now been developing alternative materials that can provide the same functionality, and light elements are recently being considered as a viable solution. As one of the approaches in these researches, the mixed anion compounds are paid attention [3, 4]. The perovskite ABO$_2$N has been studied extensively in the past decade because they offer the advantages of both oxides and nitrides [5, 6]. Oxynitrides have a smaller band gap than the original oxide and show unique electrical and optical properties [7, 8]. Among these strategies, ferroelectric Sr$_x$Ca$_{1-x}$TaO$_2$N was discovered, which was the first ferroelectric in the oxynitride class of materials [9]. In oxynitride epitaxial thin films, the structure can be controlled by the biaxial stress from the lattice mismatch with the substrate, and the ferroelectric phase is predicted to be stable in the compressively strained thin film Sr$_x$Ca$_{1-x}$TaO$_2$N. CaTaO$_2$N is the host material of Sr$_x$Ca$_{1-x}$TaO$_2$N and it can provide useful structural information on these types of materials. Oxynitride thin films have only been successfully synthesized recently, and not much is known about their structural arrangement because it is difficult to measure with neutron diffraction due to the small volume of the thin film sample.

Inverse photoelectron holography (IPH), which is one of atomic resolution holography, can observe the three-dimensional structure around specific elements [10–12]. IPH can measure the structure of single crystals including thin films, and IPH holography revealed a significant difference in the anion sites of the related SrTaO$_2$N thin film, where the oxygen atoms were found to be more disordered than the nitrogen atoms in the SrTaO$_2$N thin film [13]. However, in this experiment, information about the cations was not obtained clearly. X-ray fluorescence holography (XFH) is another atomic resolution holography using synchrotron radiation and also measure the local structure of thin film samples [14–18]. XFH can provide the local structure around specific elements heavier than Ca clearly, and this technique have been used for several perovskite materials. XFH has been applied to perovskite oxide, and the cation displacements have been observed [19–21]. These displacements of cations are considered as important points related to their functional properties such as ferroelectricity. For oxynitrides, we thought the displacements of the cations might be related to...
their physical properties, and the measurement of the local structure of the cation is important to reveal the origin of the physical properties. Moreover, the surrounding anions can affect the position of the cations and the local structure of the cations can be the key to obtain the anion arrangement. In this research, we measured the XFH hologram of CaTaO$_2$N and investigated the correlation between the cation atoms.

**II. EXPERIMENTAL**

A CaTaO$_2$N epitaxial thin film was grown using plasma assisted pulsed laser deposition on a (001) plane of the SrTiO$_3$ substrate [22]. The size of the sample is 5 mm × 5 mm, and a thickness of the thin film was approximately 20 nm. We conducted the XFH measurements at BL13XU of SPring-8 in Japan. The Ta Lα X-ray fluorescence was analyzed by a cylindrical graphite analyzer and was detected with an avalanche photodiode detector [23]. The sample was scanned along the polar angle $\theta$ (0° ≤ $\theta$ ≤ 75°, 1° step) and the azimuthal angle $\phi$ (0° ≤ $\phi$ ≤ 360°, 0.25° step). We used the incident energy from 11.0 to 14.0 keV in steps of 0.5 keV. A total of seven holograms was recorded for obtaining good atomic images.

**III. RESULTS AND DISCUSSION**

A typical hologram is shown in Figure 1(a), which was measured at the incident energy of 11.0 keV. Observed X-ray standing wave lines marked by the red dotted lines in are an indication of a good crystallinity of the measured sample and a good accuracy of the measurement. Figure 1(b) shows the hologram calculated at the same energy with a cluster size of 50 Å. This calculated hologram has the same standing wave line pattern observed in the ex-
experimental hologram. From seven experimental holograms, we reconstructed atomic images using Barton’s algorithm [24]. Further details of the experiment can be found in Refs. 23 and 25.

Figure 2 indicates the atomic images of Ta(O, N) and Ca(O, N) planes reconstructed with Barton’s algorithm [24]. The circles indicate the ideal positions of the cation atoms [5]. Atomic images were observed at expected cation positions, and this suggests that there are no large atomic displacements from the ideal positions. In principle, since the intensities of the images are proportional to the atomic number, light elements, such as oxygen and nitrogen, are difficult to observe. On the other hand, Ca and Ta images are clearly visible in the atomic images as shown in Figure 2.

To understand the behavior of the atomic image, we reconstructed other cation images within a radius of 15 Å and plotted the image intensities as a function of the distance from the emitter, as shown in Figure 3. Note that all of the intensities were normalized with respect to the atomic number because the atomic image is proportional to it. Moreover, according to the equation of the holographic oscillation, the intensity of the reconstruction should be inversely proportional to the distance. Then, the intensity variations in Figure 3 seem to follow this rule. However, the first and second neighbor Ta images are exceptionally weaker, implying a Ta−Ta short range disorder.

Another factor that affects the atomic image intensities is fluctuations of the atomic positions, which suppress the holographic signals. Therefore, the overall intensities for Ta and Ca reflect purely the magnitudes of fluctuations. To estimate them more quantitatively, we fitted and Ca reflect purely the magnitudes of fluctuations. To estimate them more quantitatively, we fitted $f(r) = a/r$ to the experimental plots for Ta and Ca, respectively, as shown in Figure 3. The fitting parameter $a$ is related to the magnitude of atomic fluctuation of the scatterer relative to the emitter, and $r$ is the distance of the atomic image from the emitter. The obtained values of $a_{Ta-Ta}$ and $a_{Ta-Ca}$ are 3.5 and 5.8, respectively. Note that we excluded the intensities of the first and second neighbor Ta images because they are too small to put together with other data for fitting. Since the ratio of $a_{Ta-Ta}$ to $a_{Ta-Ca}$ is 0.61, it suggests that Ta fluctuation is larger than Ca one. To quantify the fluctuations, we calculated holograms with varying root mean square displacements $\sigma$. The circle marks in Figure 4(a) show $\sigma_{Ta-Ta} - \sigma_{Ta-Ca}$ plots with a fixed $a_{Ta-Ta}/a_{Ta-Ca}$ ratio of 0.61. It can be seen that $\sigma_{Ta}$ is always 0.08−0.15 larger than $\sigma_{Ca}$.

In SrTiO$_3$, which is a material with a similar structure to CaTaO$_2$N, the root-mean-square displacements of thermal vibration, $\sigma_{Ti-Sr}$ and $\sigma_{Ti-Ta}$ are 0.099 and 0.11 Å at 300 K, respectively [26]. On the other hand, assuming that $\sigma_{Ca-Ta}$ in CaTaO$_2$N takes a typical value of 0.1 Å, $\sigma_{Ta-Ta}$ becomes 0.28 Å, which is much larger than $\sigma_{Ca-Ta}$. The local charge field at the Ta position is anisotropic because N$^{3-}$ and O$^{2-}$ ions randomly occupy the anion site. Therefore, the strong positional fluctuation of the Ta ion is induced, which results in the large difference of $\sigma_{Ta-Ta}$ from $\sigma_{Ca-Ta}$ [27]. This feature is not seen in ordinary oxides, and we have suc-

**Figure 3:** The distance dependence of atomic image intensities. Circle and square symbols indicate the atomic image intensities of Ta and Ca, respectively. These points show the maximum atomic image intensity around the ideal position. Solid and dotted lines indicate, respectively, the fitting lines of the Ta and Ca atomic image intensities with $f(r) = a/r$, which is the theoretical behavior of the atomic images.

**Figure 4:** (a) The relation between $\sigma_{Ta-Ta}$ and $\sigma_{Ta-Ca}$ fluctuations which gives the atomic image intensities ratio $a_{Ta-Ta}/a_{Ta-Ca}$ of 0.63. Circles indicate the calculated points, and dashed lines are guides to the eyes. (b) The relation between the fraction ratio $x$ and $\sigma_{Ta}/\sigma_{Ca}$. The exchange fraction of Ta and Ca is given by $x$ so that the chemical formula is expressed by (Ca$_{(1-x)}$Ta$_{x}$)(Ta$_{1-x}$Ca$_{x}$)O$_2$N.
ceed in measuring the unique structure of mixed anion compounds with XFH.

Another possible scenario is the large difference of the solid curve from the dashed curve in Figure 3 is that the Ta\(^{5+}\) ion occupies not only the B site but also the A site and the Ca\(^{2+}\) ion also partially occupies the B site. In the previous XAFS study on BaCa\(_{0.01}\)Ta\(_{0.9}\)O\(_{2.97}\) [28], it was found that the doped Ca ion can occupy the B site despite having the same valence as that of the Ba\(^{2+}\) ion at the A sites. In addition, the XFH measurements on Ca-doped KTapO indicated that both A and B sites are substituted by Ca [29]. A similar situation might occur in the case of perovskite oxynitrides CaTaO\(_2\)N. Taking such a structural feature into account, we use the chemical formula (Ca\(_{1-x}\)Ta\(_x\))(Ta\(_{1-x}\), Ca\(_x\))O\(_2\)N, where x is the fraction ratio of Ca at the B site and that of Ta at A site. To estimate the fraction ratio of Ca—Ta swapping, we calculated the value x as a function of the \(\sigma_{Ta}/\sigma_{Ca}\) under the condition that the ratio of \(a_{Ta-Ta}\) to \(a_{Ta-Ca}\) is 0.61. The resulting variation is shown in Figure 4(b). When \(\sigma_{Ta}/\sigma_{Ca}\) = 1, the x is 16.4%, which is the largest possible ratio. The value of x decreases with the increase of \(\sigma_{Ta}/\sigma_{Ca}\), and it approaches down to 4% in the region of \(\sigma_{Ta}/\sigma_{Ca} > 4\). These results suggest that the small amount of Ta and Ca were exchanged, probably due to the distortion of anion sublattice consisting of O and N.

CaTaO\(_2\)N thin film is a paraelectric material [22]. In this type of sample, however, SrTaO\(_2\)N has the ferroelectric feature despite the same structure [9]. The ferroelectric feature is considered to be related to the cation displacement. In the CaTaO\(_2\)N, Ta is largely displaced while Ca exists stably in the ideal position. In other XFH experiments, the atomic displacement of the A site in the ferroelectric perovskite was observed [10]. For those reasons, the ferroelectricity in the oxynitrides can also be related to the positional stability of the cation in the A site atoms.

IV. CONCLUSION

We studied the epitaxial thin film oxynitride CaTaO\(_2\)N using X-ray fluorescence holography and succeeded in obtaining clear holograms of Ta and sharp atomic images of Ta and Ca. The relative atomic function \(a_{Ta-Ta}\), which is calculated by fitting the distance dependence of the atomic image intensity with \(I = a/r\), is much smaller than \(a_{Ta-Ca}\). From the ratio of \(a_{Ta-Ta}\) and \(a_{Ta-Ca}\), we estimated the atomic fluctuation of Ta and Ca by the simulation of XFH. We found that \(\sigma_{Ta-Ta}\) becomes 0.2 Å with the assumption of the \(\sigma_{Ta-Ca} = 0.1\) Å, which is the typical value of perovskite oxide. This large positional fluctuational of Ta indicate the local charge anisotropy caused by the surrounding O\(^2-\) and N\(^2-\) ions. As another possible explanation, a part of the Ta ions occupies the A site, which is different from the previously expected site. This result is not seen in the ordinary oxide perovskites, and this suggests XFH can be used for the structural analysis of the mix anion compounds.

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