Local Structure Analysis of Lanthanum-Doped Strontium Titanate by Means of X-Ray Fluorescence Holography

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We carried out X-ray fluorescence holography at an undulator beamline of SPring-8 to investigate the local structure around the La atoms in $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ single crystal at 297 K. The weak $\text{La } L\gamma_1$ radiation was detected separately from the radiations $\text{Ti } K\alpha_1$, $\text{Ti } K\alpha_2$ and $\text{Ti } K\beta_1$. The $\text{La } L\gamma$ holograms were collected in the inverse mode at seven incident X-ray energies from 7.00 keV to 10.00 keV. By the holograms the clear atomic images of Sr(La) and Ti are reconstructed around the La atom. On the other hand, no images of the O atoms were discriminated from the intensities of artifacts. The atomic image around the La atom demonstrates that the La atoms are substituted for the Sr atoms in the cubic perovskite structure of SrTiO_3 .

Key words: $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$, X-ray fluorescence holography, $\text{La } L\gamma_1$, local structure analysis

1. INTRODUCTION

Lanthanum-doped strontium titanate $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ is electron-conductive [1]. The electrons excess due to substituting La^{3+} for Sr^{2+} are doped into the conduction band composed of the Ti-3d state, when Ti^{4+} turns into Ti^{3+} . $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ has been recently studied as thermoelectric materials of high Seebeck coefficients and applied as conductive substrates of high- T_c superconductor films [2]. From a standpoint of fundamental science, the effect of electron doping on the antiferrodistortive phase transition of SrTiO_3 has been studied [3, 4]. SrTiO_3 undergoes the second order structural phase transition at $T_a=105$ K [5]. The cubic perovskite structure with $Pm3m$ (Fig.1) changes through the softening and condensation of the R_{25} phonon mode into a tetragonal one that is organized by the network of antiferrodistortively rotated TiO_6 octahedra [6]. The rotation angle of the TiO_6 octahedra around the $\langle 100 \rangle$ axis corresponds to the order parameter of the phase transition [5]. In the case of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ [3, 4], T_a shows the large increase from 105 K at $x=0$ to 200 K at $x=0.05$ and the saturated order parameter from 2.37° at $x=0$ to 3.64° at $x=0.05$. This should be understood on the basis of the crystal structure change from $x=0$ to $x=0.05$ above T_a . The average crystal structures of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ with $x \leq 0.2$ showed that La atoms are substituted for Sr atoms [7]. However, we need to investigate the arrangement of Sr(La) atoms and TiO_6 octahedra around La atoms in the sublattices constructed, respectively, by Sr(La) atoms and Ti atoms above T_a [4].

X-ray fluorescence holography (XFH) is a powerful method for determining three-dimensional (3D) local atomic arrangements around a specific fluorescing atom. By use of third-generation synchrotron facilities, 3D atomic images in thin films, doped crystals, mixed crystals and quasicrystals have been obtained [8]. Nowadays, synchrotron X-rays generated from an undulator have made it possible to perform XFH using K radiations of a thin film containing a small amount of

dopant, e. g. XFH of $\text{ZnSnAs}_2\text{:Mn}$ (7 at. %) using the $\text{Mn } K\alpha$ radiation [9]. In the present study, therefore, we have performed XFH of $\text{Sr}_{1-x}\text{La}_x\text{TiO}_3$ using the $\text{La } L\gamma_1$ radiation to obtain the local structure around the La atoms above T_a .

2. EXPERIMENTAL

We used the (001) plate cut out from a Verneuil-grown $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ single crystal. The $\text{La } L\gamma_1$ radiation emitted from the plate, of which the intensity is the weakest among the radiations $\text{La } L\alpha_1$, $\text{La } L\alpha_2$, $\text{La } L\beta_1$ and $\text{La } L\gamma_1$, was used in the present XFH ($\text{La } L\gamma$ XFH). The $\text{La } L\gamma_1$ radiation was completely separated from the

Fig.1 Perovskite structure of SrTiO_3 with the space group $Pm3m$ in the high temperature phase. Eight unit cells are illustrated around the Sr atom located at the origin. The red spheres represent the Sr atoms, the blue ones the O atoms and the green ones the Ti atoms. The yellow planes represent the $z=0$ and the $z=\frac{1}{2}$ planes displayed, respectively, in Figs. 5 and 6.

Fig.2 Energy dependence of the mass absorption coefficient μ/ρ of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ over the range from 4 keV to 11 keV. The energies of the fluorescent X-rays and the absorption edges of La and Ti atoms are marked. The ratio among the intensities of the radiations $\text{La } L\alpha_1$, $\text{La } L\alpha_2$, $\text{La } L\beta_1$ and $\text{La } L\gamma_1$ is 100:11:60:9. Seven X-ray energies used in the $\text{La } L\gamma$ XFH are indicated by the blue arrows.

strong radiations $\text{Ti } K\alpha_1$, $\text{Ti } K\alpha_2$ and $\text{Ti } K\beta_1$ and focused properly by our toroidal graphite energy analyzer. The energies of the fluorescent X-rays and the absorption edges of La and Ti atoms are marked on the mass absorption coefficient μ/ρ of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ in Fig.2.

We performed $\text{La } L\gamma$ XFH at the undulator beamline BL09XU of the SPring-8. The $\text{La } L\gamma$ holograms were collected in the inverse mode at seven incident X-ray energies 7.00, 7.50, 8.00, 8.50, 9.00, 9.50 and 10.00 keV.

Fig.3 Scheme of the $\text{La } L\gamma$ hologram measurement system.

They are indicated by the blue arrows in Fig.2. At each X-ray energy, X-ray beam was irradiated onto the (001) surface of the (001) plate mounted on a goniometer. The plate was rotated around two axes of the azimuthal angle φ and the polar angle θ depicted in Fig.3. The $\text{La } L\gamma_1$ radiation emitted from the plate was separated from the other fluorescent X-rays and focused on the APD detector by the toroidal graphite energy analyzer [10]. The detector angle was fixed at 45° normal to the (100) surface. The measurement was made in steps of 0.300° in the range of $0^\circ \leq \varphi \leq 360^\circ$ and in steps of 1.00° in the range of $0^\circ \leq \theta \leq 75^\circ$ for 3 h at each X-ray energy. The complete hologram ($0^\circ \leq \varphi \leq 360^\circ$ and $0^\circ \leq \theta \leq 180^\circ$) was obtained at each X-ray energy by extending the measured data by the symmetry operations with respect to the fourfold rotation axes parallel to the [001], the [010] and the [100] axes and the mirror plane parallel to the (100) plane. This operation strengthened the contrast of each hologram.

3. RESULTS

3.1 Hologram

We obtained seven holograms collected at seven incident X-ray energies. Figure 4 shows an example of the $\text{La } L\gamma$ hologram obtained at the incident X-ray energy of 7.00 keV. The hologram is described by an orthographic projection of which the center points to $\theta=0^\circ$ and coincides with the direction parallel to the [001] axis. The amplitude of the holographic oscillations is large in the strongly contrasted regions in the figure. The strong X-ray standing wave lines indicate a good crystallinity of the $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ crystal. The hologram exhibits the following symmetry elements, the fourfold rotation axis along the [001] axis, the mirror planes on the {100} and the {110} planes, the threefold rotation axes along the $\langle 111 \rangle$ directions and the twofold axes along the $\langle 110 \rangle$ directions. The Barton algorithm was applied to seven holograms to reconstruct the 3D

Fig.4 The complete $\text{La } L\gamma$ hologram of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ single crystal obtained at the incident X-ray energy of 7.00 keV at 297 K. The hologram is described by an orthographic projection centered at $\theta=0^\circ$.

Fig.5 The atomic image of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ around the La atom at the origin on the $z=0$ plane reconstructed by La $L\gamma$ XFH at 297 K. The red circles represent the positions of the 3rd and the 5th neighboring Sr(La) atoms, and the blue ones those of the 1st neighboring O atoms in the cubic perovskite structure.

atomic images in which the appearance of artifacts, that is, ghost images was suppressed [11].

3.2 Atomic image

The 3D atomic image of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ around the La atom at 297 K was reconstructed by the holograms. In this section, the atomic image around the La atom is displayed on the $z=0$ and the $z=\frac{1}{2}$ planes within four unit cells depicted in Fig.1.

Figure 5 shows the atomic image around the La atom centered on the $z=0$ plane depicted in Fig.1. The intensity of the atomic image is proportional to the square of an electron density. The horizontal and the vertical axes ranging from -5 to 5 Å represent the [100] and the [010] directions, respectively. The dashed lines represent the intersections between the $z=0$ plane and the (100) planes or between the $z=0$ plane and the (010) planes. The averaged value of the lattice spacing is 3.907 Å, which was measured in $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ by X-ray powder diffraction [1]. The strong atomic images of 3rd and 5th Sr(La), which are the 3rd and the 5th nearest neighbors of the La atom, were seen within the red circles representing the Sr sites in the cubic perovskite structure. The weak images outside the red circles are artifacts. On the other hand, no atomic images of 1st O, which are the nearest neighbors of the La atom, are seen within the blue circles representing the face centers of the perovskite structure. Atomic images of 1st O were not discriminated from the intensities of artifacts lower than 0.1. Figure 5 shows that the size of the unit cell including the La atom is slightly larger than that of the average unit cell with the lattice constant of 3.907 Å. The figure also demonstrates that the La atoms are

Fig.6 The atomic image of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ around the $00\frac{1}{2}$ on the $z=\frac{1}{2}$ plane reconstructed by La $L\gamma$ XFH at 297 K. The green circles represent the positions of the 2nd neighboring Ti and the blue ones those of the 1st and the 4th neighboring O atoms in the cubic perovskite structure.

substituted for the Sr atoms in the cubic perovskite structure of SrTiO_3 .

Figure 6 shows the atomic image around the point $00\frac{1}{2}$ on the $z=\frac{1}{2}$ plane depicted in Fig.1. The axes and the lattice spacing are the same with those in Fig.5. The atomic images of 2nd Ti, which are the 2nd nearest neighbors of the La atom, are seen within the green circles located at the body centers of the perovskite structure. The intensities of the atomic images of 2nd Ti are weaker than those of 3rd and 5th Sr(La) in Fig.5, because the atomic scattering factor of Ti is smaller than that of Sr(La). The weak images outside the green circles are artifacts. On the other hand, no atomic images of 1st and 4th O were discriminated from the intensities of artifacts lower than 0.1 within the blue circles in Fig.6.

4. DISCUSSION

We modeled a cluster of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ crystal and simulated the La $L\gamma$ XFH with the same energies as the experiment. In the cluster, the O atoms are supposed to be located just at the face centers, the Ti atoms at the body centers and the Sr atoms at the lattice points around the central La atom in the cubic perovskite structure with the lattice constant of 3.9 Å. We obtained the atomic images of the cluster which were quite similar to those shown in Figs. 5 and 6 but had the lattice constant of 3.9 Å. In the calculated atomic images, we could not discriminate the O atoms from weak artifacts, as in the experimentally obtained ones. Therefore, we attribute it mainly to the atomic scattering factor of O smaller than those of La, Sr and Ti. In the present study, we did not obtain the information on the rotation of the TiO_6 octahedra in the local structure around the La atoms. We

will experimentally investigate the temperature variations of the size and the shape of the unit cells including the La atom by La $L\gamma$ XFH and those of the TiO_6 octahedra around the La atom by EXAFS.

5. CONCLUSION

The La $L\gamma$ XFH of $\text{Sr}_{0.95}\text{La}_{0.05}\text{TiO}_3$ was successfully performed at the undulator beamline BL09XU of SPring-8. The clear atomic images of Sr(La) and Ti were reconstructed around the La atom. However, no atomic images of O were discriminated from artifacts. The local structure around the La atoms demonstrates that the La atoms are substituted for the Sr atoms in the cubic perovskite structure of SrTiO_3 .

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