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# Crystal structure and microwave dielectric properties of $SrTiO_3$ doped $LaALO_3$ single crystal grown by FZ

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**Abstract**

$(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ solid solutions reveal higher quality factor ($Q \times f$) than that of pure $LaAlO_3$. We propose the use of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ single crystals for a substrate of high temperature superconductive (HTS) filters. The single crystal of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ ($x = 0.005$, 0.2) was grown by using a floating zone (FZ) method to investigate the relationship between the microwave dielectric properties and the crystal structure. Analysis of the grown $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ crystal was performed using a X-ray diffraction method. Although the crystal structure of pure $LaAlO_3$ is trigonal ($R\bar{3}m$, no. 166), the $SrTiO_3$ doped $LaAlO_3$ had stabilized cubic symmetry ($Pm\bar{3}m$, no. 221), which corresponds to high temperature phase of pure $LaAlO_3$. The refined structure of $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ exhibited ideal perovskite structure with the angle between O–B–O of 90.0°. This is related to improvement of $Q \times f$ value of $LaAlO_3$.


*Keyword:* Floating zone method; HTS filter; Microwave dielectric properties; Single crystal

## 1. Introduction

In recent years, attention has increased on mobile telecommunication. Developments of wireless communication systems have needed a demand for substrate materials of filters for base stations. In particular, high performance high temperature superconductive (HTS) filter is one of the band-pass-filter that exhibits minimum insertion loss, which is important for next generation's wireless communicating systems. However, there is a problem that the loss of the filters increases with dielectric loss of substrates printing strip lines. A possible candidate of the substrate for HTS filters is $LaAlO_3$. However, dielectric loss of the $LaAlO_3$ is still large. It has been found that substitution of $SrTiO_3$ to $LaAlO_3$ improves the dielectric loss of $LaAlO_3$.[1,2] Furthermore, the single crystal of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ should reveal smaller dielectric loss compared to the ceramics, suggesting that the single crystal is more appropriate for high performance HTS filters.

In this paper, we tried to prepare the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ single crystals by using a FZ method to investigate the structure of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ single crystal. This method is effective for preparation of crystals of high melting point. Because the high melting point of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ is more than 1800 °C, FZ method is appropriate to obtain the single crystal. The crystal structure of the grown sample $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ was refined by using a X-ray diffraction method. Based on the crystal structure, microwave dielectric properties of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ were discussed.

## 2. Experimental

### 2.1. Feed rods preparation

High purity $La_2O_3$ (>99.9 mol%), $Al_2O_3$ (>99.9 mol%), $TiO_2$ (>99.9 mol%) and $SrCO_3$ (>99.9 mol%) were used as raw materials for feed rod preparation. The $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ ceramics were prepared by the conventional mixed-oxide reaction method. The initial materials were mixed according to the stoichiometric ratio with distilled water. After drying, the powder mixture was calcined at 1400 °C for 4 h. The feed rod with a

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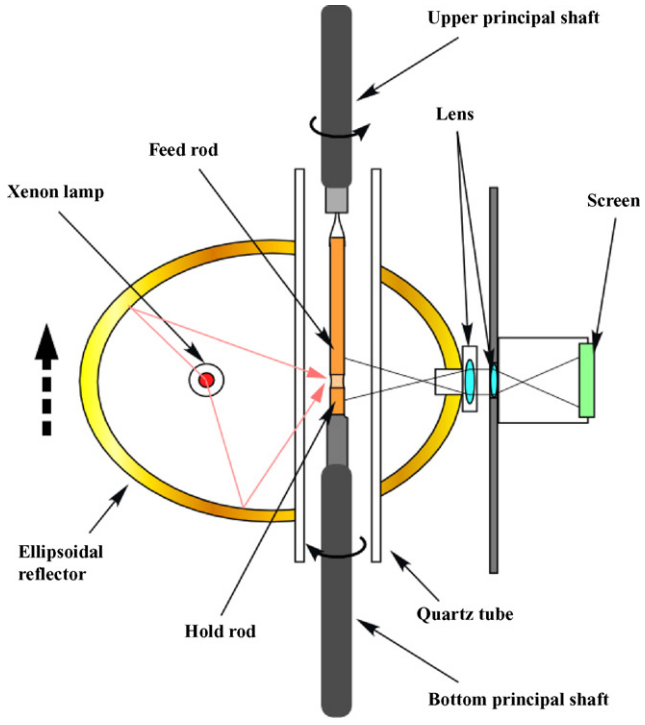


Fig. 1. Cross-sectional schema of floating zone growth furnace.

circular and columnar for 8 mm diameter and 50 mm length was prepared in a silicon rubber mold using a cold isostatic pressure of approximately 200 MPa. Then, the feed rods were sintered at 1700 °C for 20 h. A single-phase purity and the structure of the sintered materials were confirmed by powder X-ray diffraction method (Phillips; X'Pert MPD).

### 2.2. Floating zone method

FZ furnace was an infrared convergence-type image furnace with single ellipsoid mirror (NEC Co., Japan: SC-30XS-MP). Xe arc lamp of 2 kW was set at the focal point of ellipsoid as infrared source. Fig. 1 shows a cross-sectional schema of a typical crystal growth furnace. The sintered feed rod was suspended from the upper shaft and a seed crystal was fixed to the lower shaft. We used $LaAlO_3$ single crystal wafer with (1 0 0) crystallographic orientation of pseudo-cubic unit cell as seed crystal. The rotation rate was 60 rpm for both the feed rod and the feed crystal. The growth rate was varied in the range from 7 to 20 mm/h in air.

### 2.3. Crystal structure analysis

The $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ crystal structure analysis was performed. The single crystal X-ray diffraction data were recorded by using a single crystal diffractometer with imaging plate (Rigaku; R-AXIS RAPID). The structural parameters were refined by a full-matrix least-squares method that is termed RADY.[3] For comparison, the X-ray powder diffraction of the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ ceramics was also conducted using RIETAN-2000 program.[4]

Table 1
Microwave dielectric properties of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ ceramics ($x = 0$, 0.005, 0.2)

| | $\varepsilon_r$ | $Q \times f$ (GHz) |
|---|---|---|
| $LaAlO_3$ | 20 | 63,000 |
| $(La_{0.995}Sr_{0.05})(Al_{0.995}Ti_{0.05})O_3$ | 24 | 80,000 |
| $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ | 28 | 149,000 |

## 3. Results and discussion

### 3.1. $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ crystal grown by FZ

The photographs of $LaAlO_3$, the $(La_{0.995}Sr_{0.005})(Al_{0.995}Ti_{0.005})O_3$ and the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ crystal grown by FZ method at growth rate of 7 and 20 mm/h are shown in Fig. 2. In order to avoid crack or defect crystal, the used sintered rod should have a high density and homogeneity. However, several cracks were observed in the $(La_{0.995}Sr_{0.005})(Al_{0.995}Ti_{0.005})O_3$ or $LaAlO_3$ single crystal. The $LaAlO_3$ and $(La_{0.995}Sr_{0.005})(Al_{0.995}Ti_{0.005})O_3$ crystals exhibit a reddish brown color. The color presumably results from oxygen deficiency because the crystals were grown in air.[5,6] On the other hand, the color of $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ single crystal was characterized by deep green.

### 3.2. Crystal structure and microwave dielectric properties

Table 1 lists the microwave dielectric properties of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ ceramics obtained by using conventional ceramic fabrication method.[2] The $Q \times f$ value of $LaAlO_3$ was significantly modified by substitution of $SrTiO_3$. Shimada et al.[2] have investigated the dielectric properties of the $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ ceramics by using far infrared reflectivity spectra. According to their report, the increase of $Q \times f$ value and permittivity ($\varepsilon_r$) are related to the change in loss lattice vibration modes. This fact indicates that the crystal structure effected intrinsic dielectric loss. To verify the effect of crystal structure on microwave dielectric properties, we carried out the crystal structural refinement. The structural parameters of the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ single crystal, $R$-factor and weighted $R$-factor are listed in Table 2. We also refined structural parameter of the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ ceramics by Rietveld refinement (Table 3). From the analysis result, we confirmed that $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ possesses a cubic structure ($Pm\bar{3}m$,

Table 2
Structural parameters of $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ refined by X-ray single crystal analysis

| | Site | $g$ | $x$ | $y$ | $z$ | $B$ (Å) |
|---|---|---|---|---|---|---|
| La | 1$a$ | 0.016667 | 0 | 0 | 0 | 0.266(55) |
| Sr | 1$a$ | 0.004173 | 0 | 0 | 0 | 0.266 |
| Al | 1$b$ | 0.016667 | 1/2 | 1/2 | 1/2 | 0.076(87) |
| Ti | 1$b$ | 0.004173 | 1/2 | 1/2 | 1/2 | 0.077 |
| O | 3$c$ | 0.062500 | 1/2 | 1/2 | 1/2 | 1.120(63) |

$R = 2.68\%$; $R_{wt} = 3.13\%$; S.G.: $Pm\bar{3}m$, no. 221, cubic, $a = 3.8173$, $V = 55.62485$ Å.

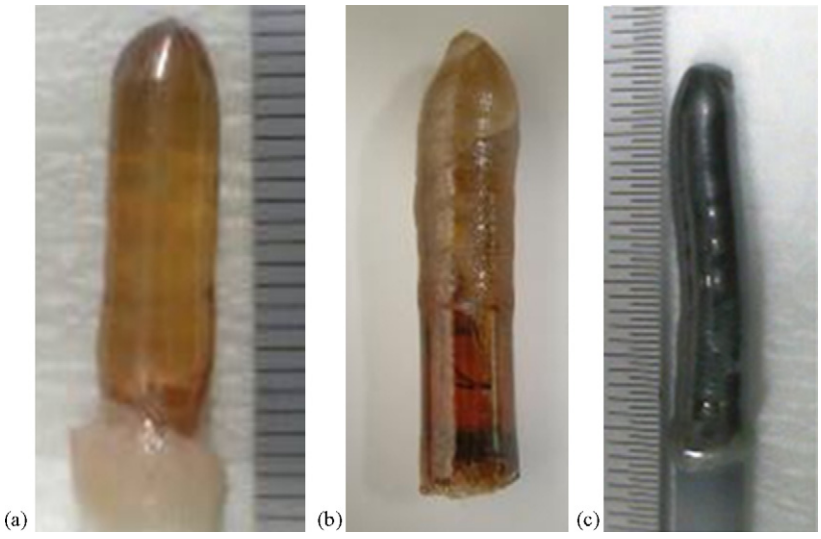

Fig. 2. Photographs of single crystals grown by FZ: (a) $LaAlO_3$ (20 mm/h), (b) $(La_{0.995}Sr_{0.005})(Al_{0.995}Ti_{0.005})O_3$ (7 mm/h) and (c) $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ (20 mm/h).

Table 3
Structural parameters of $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ refined by Rietveld analysis

| | Site | $g$ | $x$ | $y$ | $z$ | $B$ (Å) |
|---|---|---|---|---|---|---|
| A–La | 1*a* | 0.8 | 0 | 0 | 0 | 0.928(29) |
| A–Sr | 1*a* | 0.2 | 0 | 0 | 0 | 0.928 |
| B–Al | 1*b* | 0.8 | 1/2 | 1/2 | 1/2 | 0.702(37) |
| B–Ti | 1*b* | 0.2 | 1/2 | 1/2 | 1/2 | 0.702 |
| O | 3*c* | 1.0 | 0 | 1/2 | 1/2 | 1.349(57) |

$R_{wp} = 10.44\%$; $R_I = 3.96\%$; $R_F = 2.18\%$; $S = 1.5247$; S.G.: $Pm\bar{3}m$, no. 221, cubic, $a = 3.83120(1)$, $V = 56.2347(5)$ Å.

no. 221) where Sr and Ti ions are soluble in both A- and B-sites of $LaAlO_3$, respectively. The crystal data of $LaAlO_3$ are trigonal ($R\bar{3}m$, no. 166), $a = 5.357$ Å and $\alpha = 60°6'$, indicating that the crystal structure of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$ solid solutions was changed by substituting $SrTiO_3$ into trigonal ($LaAlO_3$) to cubic ($(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$).

In order to investigate the variation of the permittivity ($\varepsilon_r$) by substituting $SrTiO_3$, the bond length and site volumes were calculated by using the refined structural parameter.[7] The results of bond length and site volumes of the $LaAlO_3$ or $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ are listed in Table 4. It shows that the volume of $BO_6$ octahedra of $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ is larger than that of the $LaAlO_3$. It is considered that the increase of the permittivity results from the increase of the volume of $BO_6$ octahedra, owing to higher ionic polarizations. However, the $Q \times f$ value was not contributed to the site volume of $BO_6$ octahedra. We also calculated the angle between O–B–O[7] of the $LaAlO_3$ and the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ by using the refined crystal parameters. The estimated angle is also listed in Table 4. The angle between O–B–O of the $LaAlO_3$ exhibits 89.840° or 90.160°, on the other hand, the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ exhibits 90.0°. It means that the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ has an ideal perovskite structure, hence, each ion at A- and B-sites keeps valance between Coulomb and repulsion force. Consequently, the response against external electric field becomes quicker because there is no obstruct factor. Therefore, improvement of $Q \times f$ value for $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ is possible.

Table 4
Bond length, site volumes and angle between O–B–O of $(La_{1-x}Sr_x)(Al_{1-x}Ti_x)O_3$

| | | | |
|---|---|---|---|
| Bond length (Å) | La–O | 2.5294 | 2.6992(8) |
| | Al–O | 1.8986 | 1.9086(7) |
| Site volume (Å$^3$) | A-site | 38.824 | 46.3541 |
| Angle between O–B–O (°) | B-site | 5.3758 | 9.2702 |
| | | 89.840 or 90.160 | 90 |

## 4. Conclusions

The single crystals of the $LaAlO_3$, the $(La_{0.995}Sr_{0.005})(Al_{0.995}Ti_{0.005})O_3$ and the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ were prepared by using FZ method. The crystal structure of the $(La_{0.8}Sr_{0.2})(Al_{0.8}Ti_{0.2})O_3$ was determined as $Pm\bar{3}m$ by both X-ray single crystal analysis and Rietveld refinement. The relationship between improvement of microwave dielectric properties and crystal structure is discussed. The increase of the permittivity is related to the site volume of $BO_6$ octahedra and the $Q \times f$ value is related to response against external electric field.

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