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Microwave dielectric properties of lanthanum aluminate ceramics and single crystal

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Abstract

Single crystal and ceramics of $LaAlO_3$ were prepared by a Czochralski method and conventional solid phase reaction, respectively, using high purity reagents. Far infrared reflectivity spectra for single crystals and ceramics of $LaAlO_3$ were measured and eigenfrequencies and damping constants of transverse and longitudinal optical modes were evaluated in order to discuss variations in the dielectric properties. The observed reflectivity spectra were fitted by four IR active modes (predicted by factor group analysis) in order to calculate the vibration eigenfrequencies and damping constants. Differences in dielectric loss were found between the two kinds of single crystals, having different crystal orientations. It was inferred that the difference in dielectric loss was due to difference in cut off frequencies of these single crystals. The loss obtained from the IR reflectivity of the ceramics was used to evaluate the extrinsic loss in the ceramics.

Keywords: Microwave properties; Dielectric properties; Perovskites

1. Introduction

Recent studies of materials for high frequency wireless communication are focused dielectric loss. Many high Q materials are used for dielectric substrate, filter and several wireless devices. In particular, the strip line filter, using high temperature superconductor (HTS), is expected to be a high performance microwave filter in base stations. Since the strip line of the HTS filter is constructed from superconducting materials, the losses from the conductor can be ignored because of its high electrical conductivity. Therefore, the loss of the filter results from the loss of the dielectric materials used as a substrate. Lanthanum aluminate ($LaAlO_3$; LAO) is a candidate substrate for the HTS filter. It is necessary to reduce the dielectric loss of the LAO in order to improve the properties of the HTS filter.

It is known that the LAO has a rhombohedral crystal structure, which is similar to a slightly distorted cubic structure.[1] The microwave absorption in single crystal LAO has been thoroughly investigated by Zuccaro et al.[2] They pointed out that loss of the LAO single crystal is due to microwave absorption by phonons and relaxation of dipoles brought about by defects in the crystal. The dielectric loss of LAO ceramic was compared to that of single crystal by Alford et al.[3] They observed the same behavior as Zuccaro in plots of loss versus temperature, with the peak due to relaxation of dipole in both ceramics and single crystal. Alford et al. found that the loss of ceramics was higher than that of the single crystal by an order of magnitude. The fundamental dielectric loss theory of the single crystals was given by Stolen–Dransfeld[4] and Sparks–King–Mills[5]; Zuccaro adapted their explanation to interpret the dielectric loss of LAO. For the microwave frequencies which is much lower than the cut off frequency (ω_c) at the Brillouin zone boundary and reststrahlen frequency (ω_f), the dielectric loss associated the two-phonon difference process is given by

$$\tan\delta \cong \phi_3^2 \frac{h\omega}{k_B T}\left[\exp\left(\frac{h\omega_i}{k_B T}\right)-1\right]^{-1} \times \left\{\left[\exp\left(\frac{h\omega_i}{k_B T}\right)-1\right]^{-1}+1\right\} \times \left[\tan^{-1}\frac{\omega_f}{\gamma}-\tan^{-1}\frac{\omega_c}{\gamma}\right] \quad (1)$$

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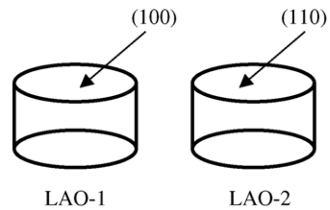

Fig. 1. Two forms of LAO single crystals.

where ϕ_3, ω, k_B, T, h, ω_i, γ are the third derivative of the lattice potential, the frequency, Boltzmann constant, the temperature, Plank constant, the *i* mode phonon frequency and the linewidth of the two phonons, respectively. In the investigation by Zuccaro, the dielectric losses were evaluated by a cavity method at microwave frequency, but ω_f and ω_c were not evaluated. Infrared spectroscopy is the most appropriate method for the observation of the reststrahlen mode of the LAO.

In the present study two kinds of LAO single crystals were prepared and far infrared reflectivity was obtained. The data for the single crystals were compared with that of LAO ceramics.

2. Experimental procedure

A $LaAlO_3$ single crystal was grown by the Czochralski method and cut to disc shape, 10 mm in diameter. Single crystal discs having (1 0 0) and (1 1 0) surfaces were prepared, denoted as LAO-1 and -2, respectively (Fig. 1); the surfaces were treated by optical polishing. $LaAlO_3$ ceramics (LAO-C) were prepared by a conventional mixed-oxide reaction method. To prepare the LAO-C so that it was in an appropriate state for far infrared measurement, high purity reagents of lanthanum and aluminum oxides were employed. These oxides were ball milled using zirconia balls in deionized water and then calcined for 4 h at 1673 K in air. The calcined powder was subjected to ball-milling again, and then the powders were pressed to form pellets 12 mm in diameter. The pellets were sintered at 1953 K for 50 h using an electric furnace.

X-ray diffraction analysis was performed to confirm that no second phases were formed in the LAO-C matrix. The dielectric properties of the samples were measured by the Hakki and Coleman open resonator method in the microwave range, using a network analyzer (HP8720D).

The surfaces of the LAO-C were wet polished using a 1 μm diamond slurry. By this the surface roughness (Ra) was reduced to less than 5×10^{-4} μm. After polishing the ceramics was washed with acetone in an ultrasonic bath to eliminate the influence of the surface impurities on the IR measurements. Far-infrared reflectivity spectra of the polished samples were measured at room temperature using a fourier transform infrared spectroscope (FT-IR; Bruker IFS 66 V) having a SiC glow bar lamp and Au reflector as the measurement reference. The incident angle of radiation was 11° and the

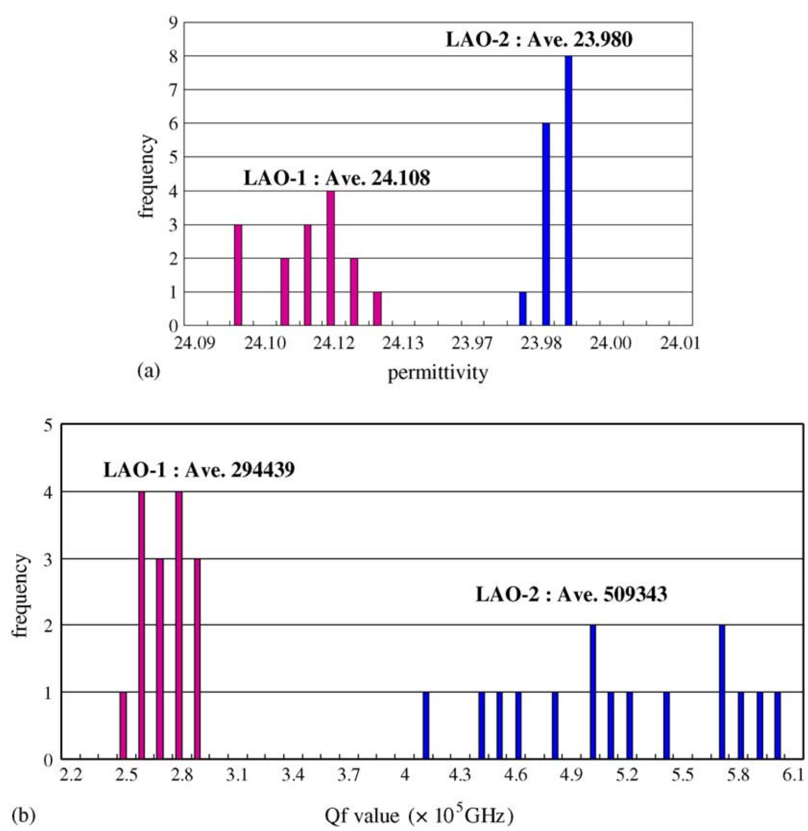

Fig. 2. (a) Relative permittivity distribution of LAO single crystals. (b) *Q*f value distribution of LAO single crystals.

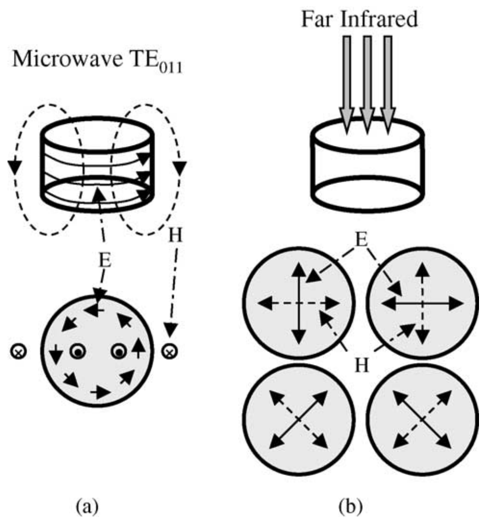

Fig. 3. Electric and magnetic field in LAO: (a) electro-magnetic field for TE_{011} mode and (b) electro magnetic field of infrared ray.

spectra resolution was 1.0 cm^{-1}. The vibration parameters were estimated by spectrum fitting method using products formula.[6,7]

3. Results and discussion

Fig. 2 shows the relative permittivity and the *Q*f value distributions of the LAO-1 and -2, respectively. Since the Hakki & Coleman open resonator method is not always sufficient for dielectric loss measurement of materials having extremely high *Q* value, the dielectric loss of a batch of samples prepared from same crystal lot was measured to increase the accuracy of the data. The average relative permittivity and *Q*f value of the LAO-C were found to be 20.66 and 69550 GHz, respectively, at microwave frequency. In comparison with the single crystal data it was found that the relative permittivity of the single crystal was higher than that of the ceramics by 16%, and *Q*f value of the single crystal was higher by an order of magnitude. This result was in good agreement with data reported by Alford et al.[3] However, there was no difference between the τ_f values for the single crystals and ceramics; their values were about −56 from −53 ppm/K, respectively. A noteworthy point for the *Q*f values is that the LAO-2 shows a significantly higher *Q*f value than the LAO-1. We utilized TE_{011} and TE_{012} resonant modes for the measurement of the *Q*f values. The electric field of these modes is parallel to the single crystal surfaces. The field for TE_{011} is illustrated in Fig. 3(a) . Therefore, it was considered that the difference in *Q*f values resulted from the direction of the electric field in the samples. Since the lattice vibration is brought about by periodic variation in the electric field, the measurement of the lattice vibration might give some information about the origin of the difference in the *Q*f values. Far infrared reflectivity of the LAO includes information about the lattice vibration. The normal modes at the center of Brillouin zone are classified from factor group analysis of the LAO (D^5_{3d}) as

$$\Gamma = A_{1u} + 4A_{2u} + 5E_u \quad (2)$$

Thus, four infrared active phonon modes are expected from Eq. (2).[8] If the infrared signal is incident on the cylindrical sample without polarization of the infrared beam as shown in Fig. 3(b), the electric field in the samples become equivalent to the electric field in the microwave measure-

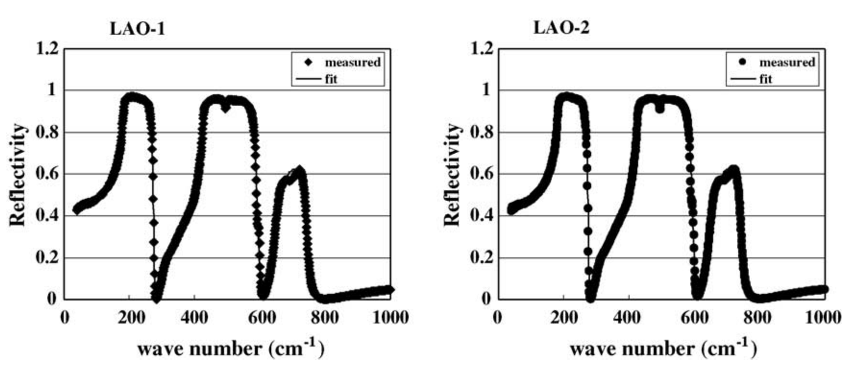

Fig. 4. Far infrared reflectivity of LAO single cryatals.

Table 1
Vibration parameters of LAO single crystals

Mode	LAO-1				LAO-2			
	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$
Eigenfrequency and damping constant (cm^{-1})								
1	182.8	5.4	276.2	4.1	184.4	5.0	276.6	4.0
2	426.5	5.4	428.9	114.9	427.0	4.6	427.0	110.9
3	430.4	131.8	596.3	12.8	430.1	126.7	598.2	12.8
4	647.3	39.4	743.8	11.6	649.3	38.4	744.6	11.8

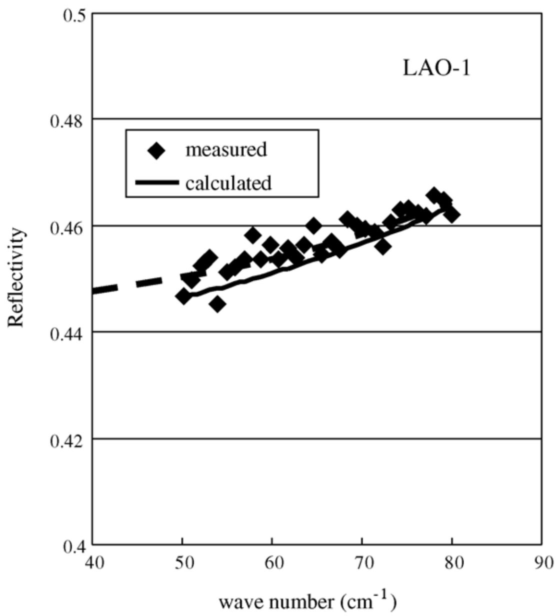

Fig. 5. Reflectivity of LAO-1 at low frequency.

ment. Fig. 4(a) and (b) show the far infrared reflectivity of the LAO-1 and -2, respectively. The spectrum fits of the data are also shown in the figures. The product formula and relation between relative permittivity and reflectivity expressed in Eqs. (3) and (4) were used in spectrum fitting.[6]

$$\varepsilon = \varepsilon_\infty \prod_{j=1}^{4} \frac{\Omega_{j\mathrm{LO}}^2 - \omega^2 + \mathrm{i}\omega\gamma_{j\mathrm{LO}}}{\Omega_{j\mathrm{TO}}^2 - \omega^2 + \mathrm{i}\omega\gamma_{j\mathrm{TO}}} \quad (3)$$

$$R = \frac{|\varepsilon^{1/2} - 1|^2}{|\varepsilon^{1/2} + 1|^2} \quad (4)$$

where ε, ε_∞, ω, and R are the relative permittivity, the relative permittivity at high frequency, the frequency and the reflectivity, respectively. $\Omega_{j\mathrm{LO}}$ and $\Omega_{j\mathrm{TO}}$ are the eigenfrequencies of the longitudinal optical (LO) and the transverse optical (TO) modes, and $\gamma_{j\mathrm{LO}}$ and $\gamma_{j\mathrm{TO}}$ are the damping constants of the LO and TO modes, respectively. Of course the $\Omega_{j\mathrm{TO}}$ associated strongly with microwave loss is equals ω_f. The vibration parameters obtained from the spectrum fitting are listed in Table 1. There was no great difference between vibration parameters for LAO-1 and -2. However, the best calculated fit spectral lines were not in exactly agreement with measurements at low frequency (less than 100 cm^{-1}), for example as shown in Fig. 5 for LAO-1. This is just an effect from the anharmonic lattice vibration. The tan δ data obtained from the measurement data were plotted as a function of frequency (Fig. 6). The ω_c values for LAO-1 and -2 were evaluated by the least squared method using Eq. (1) and calculated to be 500 and 608 GHz, respectively. These values are close to the value quoted by Zuccaro. The difference in ω_c between the LAO-1 and -2 reflects the difference in Qf values at microwave frequencies. In other words, since it is difficult for an optical phonon in material having higher ω_c to be created from an acoustic phonon at Brillouin zone boundary, the measured Qf value of LAO-2 was higher than that of LAO-1.

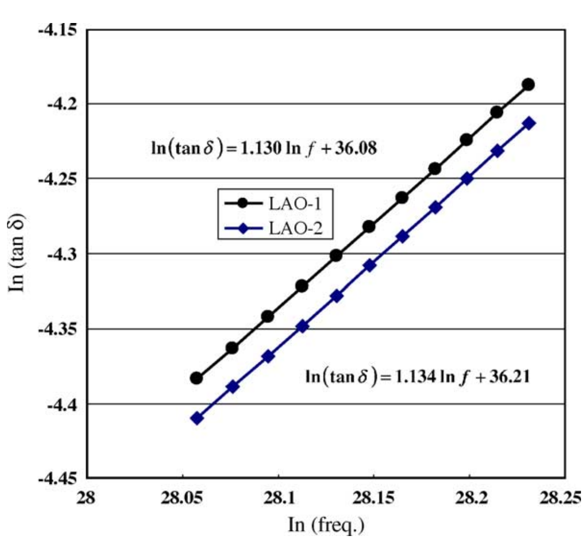

Fig. 6. tan δ as a function of frequency for LAO-1 and -2.

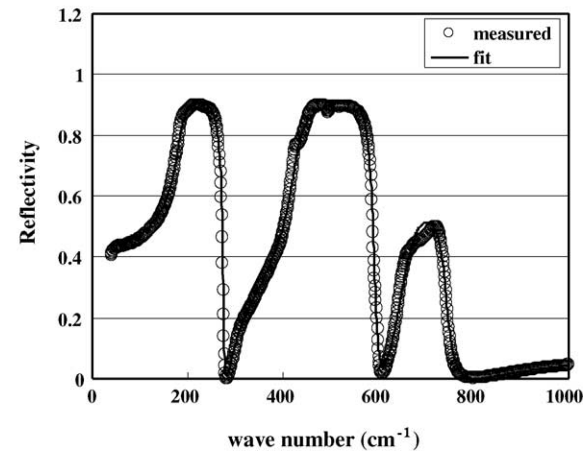

Fig. 7. Far infrared reflectivity for LAO ceramics.

Fig. 7 shows far infrared reflectivity of the LAO-C. The vibration parameters are listed in Table 2. A ripple was observed in the spectrum at 430 cm^{-1}. The damping constants are larger than those for the single crystal. The ceramics and single crystal LAO have similar intrinsic loss, so the difference in dielectric loss is due to extrinsic effect in the THz region. Plots of tan δ versus frequency for single crystal and ceramics are shown in Fig. 8. In this figure, tan δ_in and tan δ_c express the intrinsic dielectric loss, calculated from the single

Table 2
Vibration parameters of LAO ceramics

Mode	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$
Eigenfrequency and damping constant (cm^{-1})				
1	184.5	16.1	275.8	4.7
2	427.4	17.0	427.4	270.2
3	445.0	300.0	594.6	12.8
4	645.9	52.8	743.1	14.1

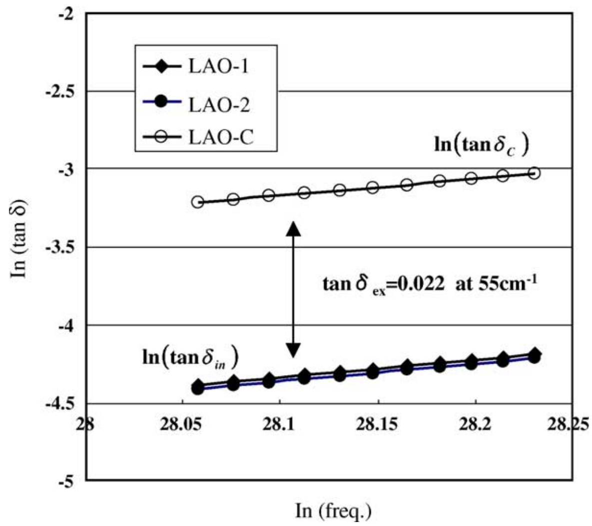

Fig. 8. Comparison of low frequency tan δ for LAO single crystals and ceramics.

crystal data, and the dielectric loss of the ceramics, respectively. Furthermore, tan δ_{ex} expresses the extrinsic dielectric loss. Since the difference between tan δ for the single crystal and the ceramics indicates the extrinsic dielectric loss of the ceramics, tan δ_{ex} can be roughly evaluated from tan δ_{in} and tan δ_{c}. Its value was calculated to be about 0.022 at 55 cm^{-1}. It is inferred that this extrinsic dielectric loss came about from the presence of grain boundaries, porosity, impurities, structural defects, etc. However, we could not discriminate between the individual loss mechanisms in the present study. The ripple, which appeared in the IR spectrum of the ceramics (Fig. 7), might indicate one kind of cause for the extrinsic loss.

4. Conclusions

In the present study, the difference between the dielectric properties of single crystal and ceramics of LAO was discussed in terms of microwave measurement data and far infrared reflectivity. We can make the following conclusions: (i) the difference in dielectric loss between LAO-1 and -2 was due to differences in their cut off frequencies and (ii) the extrinsic loss of LAO ceramics was determined to be about 0.022 at 55 cm^{-1}.

We could only find the difference in dielectric loss between single crystals and ceramics, when low frequency loss spectra were evaluated under special condition, for example the two-phonon difference process in the LAO single crystal. In order to confirm the validity of our results additional evaluations should be carried out to supplement this research, for example, neutron scattering measurements.

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