Microwave Dielectric Properties of Lanthanum Aluminate Ceramics and Single Crystal

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Abstract

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 in the single crystal and ceramics. The single crystal and the ceramics were prepared by a Czochralski method and conventional solid phase reaction using high purity reagents respectively. The observed reflectivity spectra were fitted by 4 IR active modes predicted by factor group analysis in order to evaluate the vibration eigenfrequencies and damping constants. It was found that difference in dielectric loss between two kinds of single crystals, which have the different crystal orientation along with an central axis in the cylindrical shape crystals. It was inferred that the difference in dielectric loss was due to that in cut off frequency of the single crystals. The loss obtained from the IR reflectivity of the ceramics was used to evaluate the extrinsic loss in the ceramics.

Keywords

Microwave materials

Microwave properties

Dielectric properties

Perovskites

Far-infrared reflectivity

Lattice vibration

Anharmonic term

Tow-phonon difference process

Lanthanum aluminate

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. Especially the strip line filter using high temperature superconductor□(HTS) is expected as the post high performance microwave filter in base station. Since the strip line of the HTS filter is constructed by the superconducting materials, the loss from the conductor can be ignore because of its high electric conductivity. Therefore the loss of the filter results in the loss from the dielectric materials used as a substrate. Lanthanum aluminate ($LaAlO_3$; LAO) is a candidate of the substrate for the HTS filter. It is required to decrease 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 distorts slightly from cubic structure [(1)]. The microwave absorption in single crystal of the 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. Also the dielectric loss of LAO ceramics was compared with its single crystal by Alford et al [(3)]. They observed same behavior with Zuccaro's plots of loss versus temperature for the LAO single crystal, and the peak due to relaxation of dipole were found in both ceramics and single crystal. The loss of ceramics was higher than that of the single crystal by an order of magnitude in their observation. The fundamental dielectric loss theory of the single crystals was given by Stolen - Dransfeld [(4)] and Sparks - King - Mills [(5)], and Zuccaro simplified their explanation of the dielectric loss. For the microwave frequency which is extremely lower than 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

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

…(1)

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. In the investigation by Zuccaro the dielectric losses were evaluated by a cavity method at microwave frequency, ω_f and ω_c were not evaluated. The 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 observed, and also the data of the single crystals was compared with that of LAO ceramics.

2. Experimental procedure

$LaAlO_3$ single crystal was growth by Czochralski method and was cut to the disc shape having 10 mm in diameter. The single crystal discs having (100) and (110) surfaces were prepared, which abbreviate to LAO-1 and LAO-2 respectively (Fig. 1), and 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 the far infrared measurement, high purity reagents of lanthanum and aluminum oxides were used as the raw materials. These oxides were mixed by ball mill using zirconia balls in deionized water and then calcined for 4 hours at 1673 K in air. The calcined powder was then subjected to ball-milling again, and the powders were pressed to form a pellet 12 mm in diameter. The pellets were sintered at 1953 K for 50 hours 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 Hakki & Coleman's open resonator method in the microwave range, using a network analyzer (HP8720D).

The surfaces of the LAO-C were wet polished using about 1 µm diamond slurry by which the surface roughness (Ra) was reduced to less than 5×10^{-4} µm, and then washed with acetone in an ultrasonic bath to eliminate the influence of the surface impurities on the IR measurement. Far-infrared reflectivity spectra of the polished samples were measured at room temperature using a Fourier Transform Infrared Spectroscope (FT-IR; Bruker IFS 66V) having a SiC glow bar lamp and Au reflector as the measurement reference. The incident angle of radiation was 11 ° and the 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 permittivity and the Qf value distributions of the LAO-1 and -2 respectively. Since Hakki & Coleman's open resonator method is not always sufficient for the dielectric loss measurement of the materials having extremely high Q value, the dielectric loss of some samples prepared from same product lot was measured to increase the accuracy of the data. The average permittivity and Qf value of the LAO-C were found to be 20.66 and 69550GHz at microwave frequency. In comparison with the single crystal and the ceramics, the permittivity of the single crystal was higher than that of the ceramics by 16%, and Qf value of the single crystal increased by an order of magnitude. This result was in good agreement with data reported by Alford et al [(3)]. Whereas it was found that no difference in the τf value between the single crystal and ceramics and their values were about –56 from –53 ppm/K. A noteworthy point for Qf value is that the LAO-2 shows exceedingly higher Qf value than that of the LAO-1. We utilized TE_{011} and TE_{012} resonant modes for the measurement of the Qf values. Electric field of these modes is parallel to the

single crystal surfaces as illustrated in Fig. 3 (a). Therefore it was considered that the difference in Qf values resulted in direction of the electric field in the samples. Since the lattice vibration is brought about by the electric field periodic variation, the measurement of the lattice vibration might give some information for the difference in the Qf value. Far infrared reflectivity of the LAO includes its information for the lattice vibration. The normal modes at the center of Brillouin zone is classified from factor group analysis of the LAO (D_{3d}^5) as

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

4 modes infrared active phonons are expected from equation (2) [(8)]. If the infrared is incident on the cylindrical samples without polarization of the infrared as shown in Fig. 3 (b), the electric field in the samples become equivalent to the electric field in the microwave measurement. Figs. 4 (a) and (b) show the far infrared reflectivity of the LAO-1 and 2 respectively. Also spectrum fits of these spectra are shown in same figures. The product formula and relation between permittivity and reflectivity expressed in equation (3) and (4) were used in spectrum fitting [(6)].

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

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

where ε, ε_∞, ω, and R are the permittivity, the permittivity at high frequency, the frequency and the reflectivity respectively. Ω_{jLO} and Ω_{jTO} are the eigenfrequencies of

the longitudinal optical (LO) and the transverse optical (TO) modes, and γ_{jLO} and γ_{jTO} are the damping constants of the LO and TO modes respectively. Of course the Ω_{jTO} associated strongly to microwave loss is equals ω_f. The vibration parameters obtained from the spectrum fitting are listed in Table 1. There was no great difference in vibration parameters between the LAO-1 and 2. However the calculation lines were not in exactly agreement with the measurement at low frequency less than 100 cm^{-1}, for example as shown in Fig. 5 for the LAO-1. This is just an effect from the anharmonic lattice vibration. Then the $\tan\delta$ obtained from the measurement data was plotted versus frequency as shown in Fig. 6, and ω_c of LAO-1 and 2 were evaluated by the least squared method and calculated to be 500 and 608 GHz respectively. These value are close to the value quoted by Zuccaro. The difference in ω_c between the LAO-1 and 2 is reflected that in Qf value at microwave frequency. In other words, since it is difficult that an optical phonon in the system having higher ω_c is created at Brillouin zone boundary, The Qf value of the LAO-2 was measured higher than that of the LAO-1.

Fig. 7 shows far infrared reflectivity of the LAO-C, and its vibration parameters are listed in Table 2. The ripple was observed at 430 cm^{-1}. The damping constants became bigger compared with the single crystal. The ceramics and single crystal of the LAO have the similar intrinsic loss, so their difference in dielectric loss is due to extrinsic effect in the THz region. The similar plot of $\tan\delta$ versus frequency is shown in Fig. 8. In this figure, $\tan\delta_{in}$ and $\tan\delta_c$ express the intrinsic dielectric loss, which calculated from the single crystal data, and the dielectric loss of the ceramics. Also $\tan\delta_{ex}$ express the extrinsic dielectric loss. Since the difference in $\tan\delta$ between the single crystal and the ceramics indicates the extrinsic dielectric loss of the ceramics, $\tan\delta_{ex}$ can be roughly evaluated from $\tan\delta_{in}$ and $\tan\delta_c$. Its value was calculated to be about 0.022 at 55 cm^{-1}. It is inferred that this extrinsic dielectric loss came from grain boundary, porosity, impurity,

structural defect and so on, however we could not discriminate to the individual losses in the present study. The ripple, which appeared in the IR spectrum of the ceramics, might indicate a kind of cause for the extrinsic loss.

4. Conclusions

In the present study, the difference in the dielectric properties of single crystal and ceramics of LAO was discussed from microwave measurement data and far infrared reflectivity. We can conclude as follows about the effect to dielectric loss brought about by single crystal direction and the evaluation of the extrinsic loss of the ceramics.

4.1 It was inferred that the difference in dielectric loss between LAO-1 and LAO-2 was due to that in their cut off frequencies.

4.2 The extrinsic loss of LAO ceramics was evaluated about 0.022 at 55 cm^{-1}.

We could find only the difference in dielectric loss between single crystals and ceramics, and all of the calculation values were evaluated under a special condition, for example the two-phonon difference process in the LAO single crystal. In order to confirm our results to be reasonable, some other and additional evaluations have to be carried out as a supplement research, for example as a neutron scattering measurement.

Reference

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Table 1 Vibration parameters of LAO single crystals.

	LAO-1				LAO-2			
	Eigen frequency and Damping constant (cm^{-1})							
Mode	Ω_{jTO}	γ_{jTO}	Ω_{jLO}	γ_{jLO}	Ω_{jTO}	γ_{jTO}	Ω_{jLO}	γ_{jLO}
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

Table 2 Vibration parameters of LAO ceramics.

Eigen frequency and Damping constant (cm^{-1})				
Mode	Ω_{jTO}	γ_{jTO}	Ω_{jLO}	γ_{jLO}
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

Legends

Fig.1 Two kinds of LAO single crystals.

Fig.2 Permittivity distribution of LAO single crystals.

Fig.3 Qf value distribution of LAO single crystals.

Fig.4 Temperature coefficient of resonant frequency of LAO single crystal and ceramics.

Fig. 3 Electric and magnetic field in LAO, (a) Electro-magnetic field of TE011 mode, (b) Electro magnetic field of infrared ray.

Fig. 4 Far infrared reflectivity of LAO single cryatals.

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

Fig. 6 $\tan\delta$ and frequency plots of LAO-1 and 2.

Fig. 7 Far infrared reflectivity of LAO ceramics.

Fig. 8 Comparison with low frequency $\tan\delta$ of LAO single crystal and ceramics.

Fig. 1

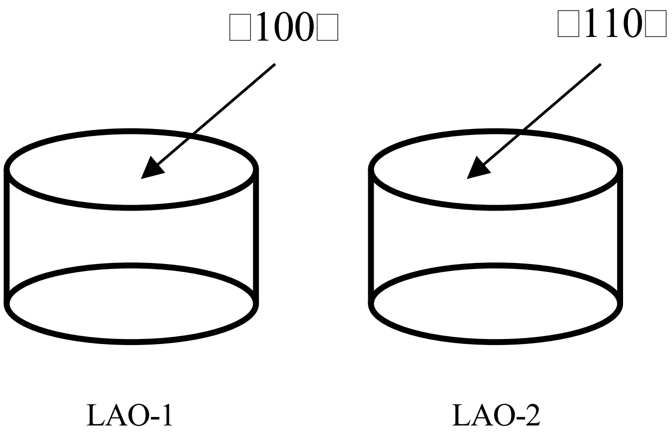


Fig. 2

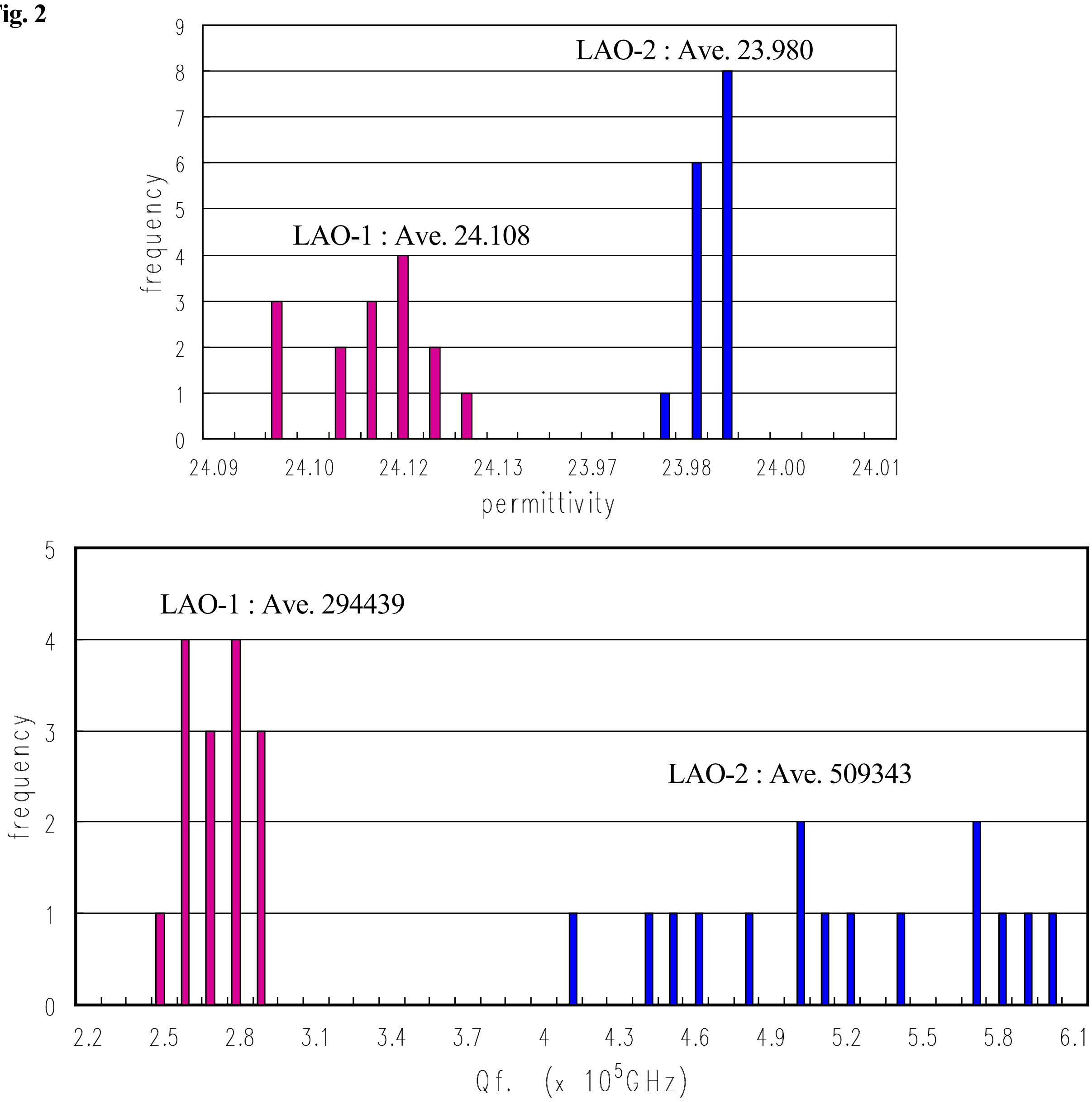

LAO-2 : Ave. 23.980
LAO-1 : Ave. 24.108
frequency
0
1
2
3
4
5
6
7
8
9
24.09
24.10
24.12
24.13
23.97
23.98
24.00
24.01
permittivity
LAO-1 : Ave. 294439
LAO-2 : Ave. 509343
frequency
0
1
2
3
4
5
2.2
2.5
2.8
3.1
3.4
3.7
4
4.3
4.6
4.9
5.2
5.5
5.8
6.1
Qf. (x 10^{5}GHz)

Fig. 3

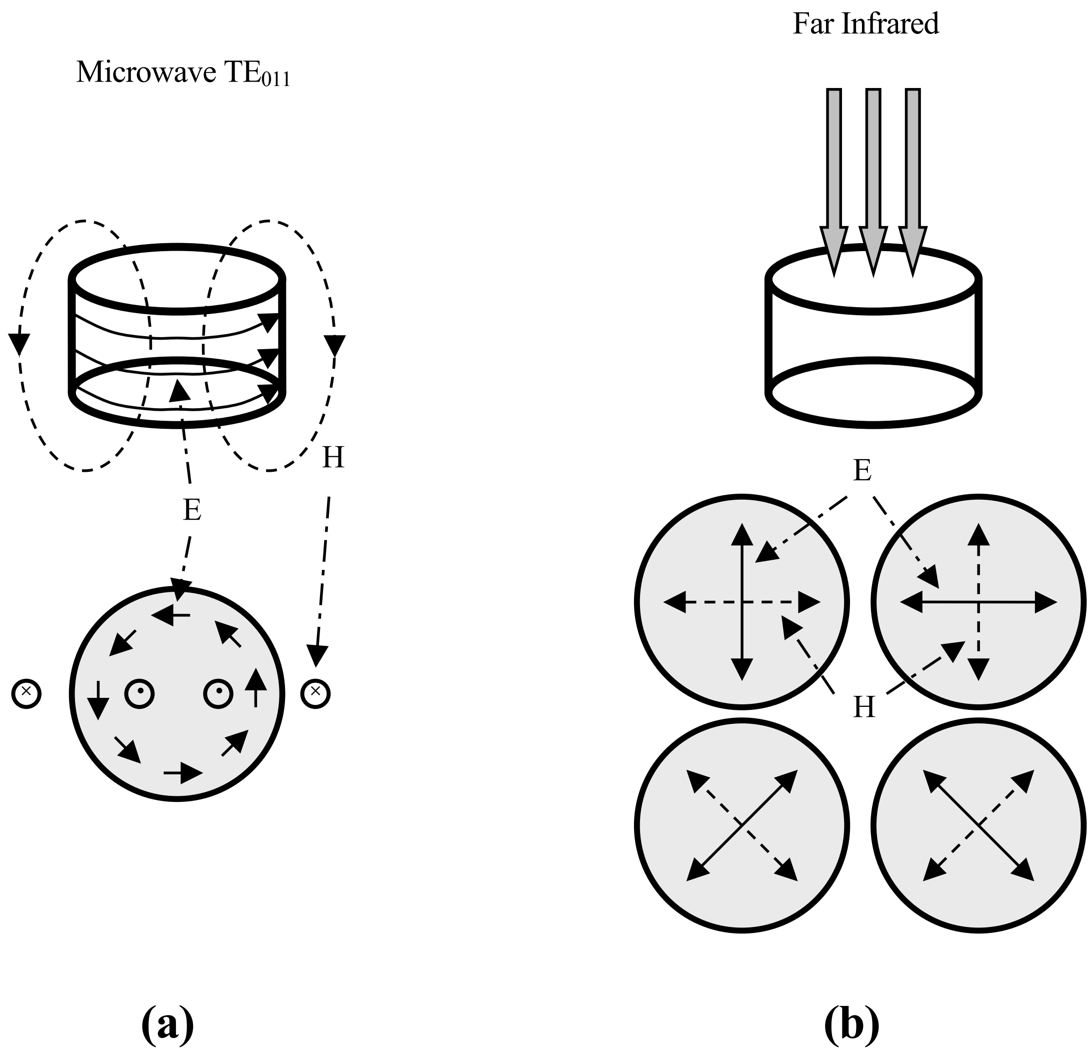
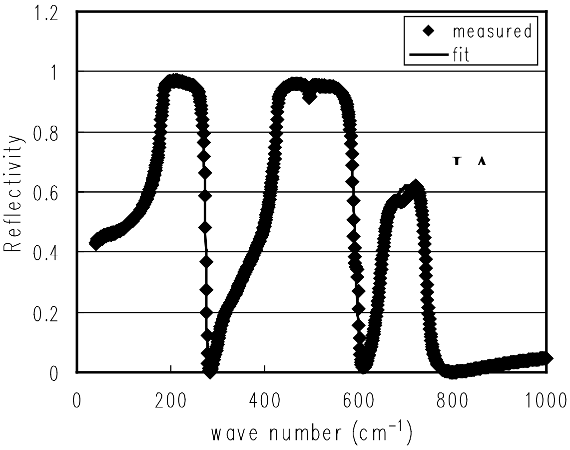


Fig. 4

LAO-1



LAO-2

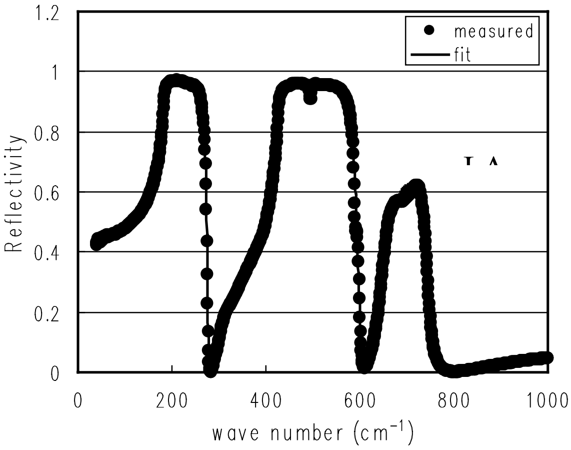
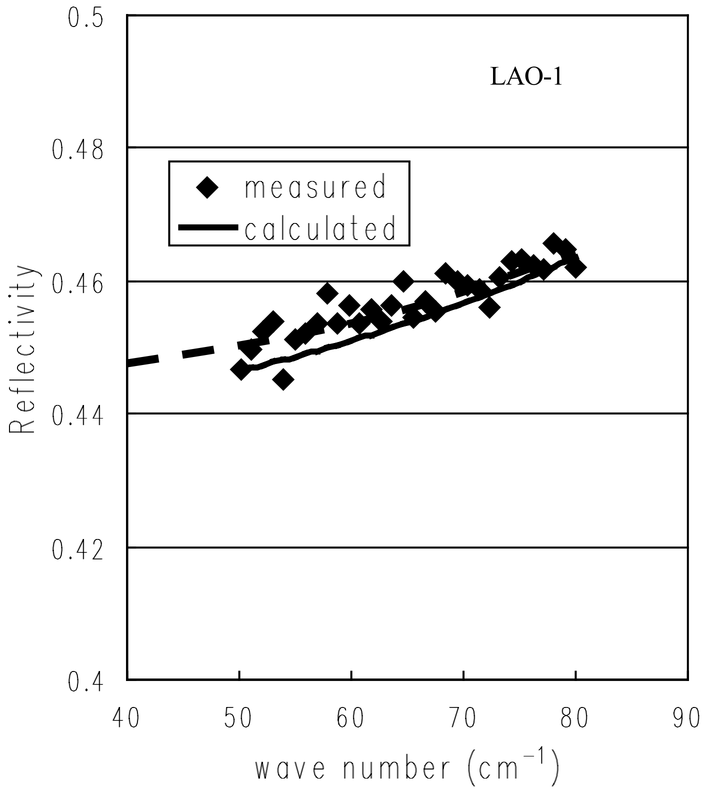


Fig. 5



LAO-1
measured
calculated
Reflectivity
0.5
0.48
0.46
0.44
0.42
0.4
40
50
60
70
80
90
wave number (cm^{-1})

Fig. 6

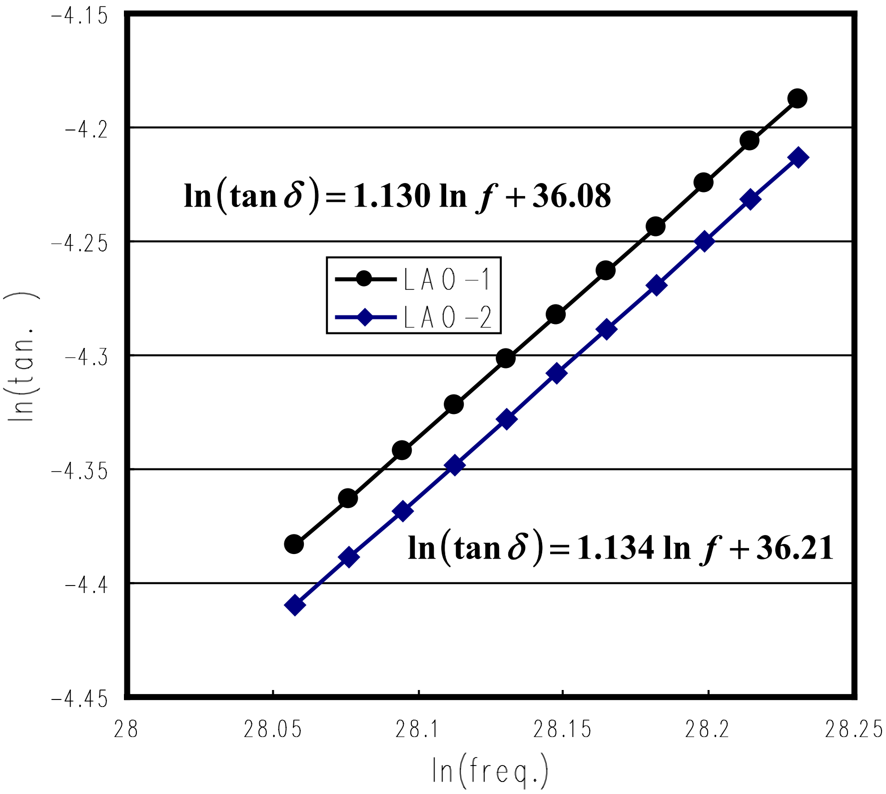
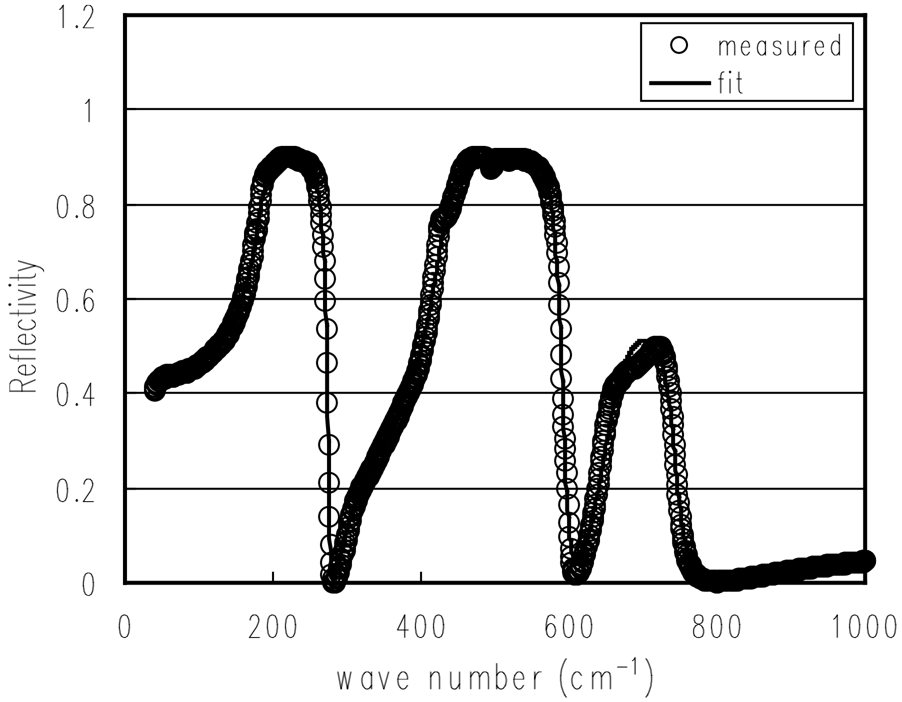
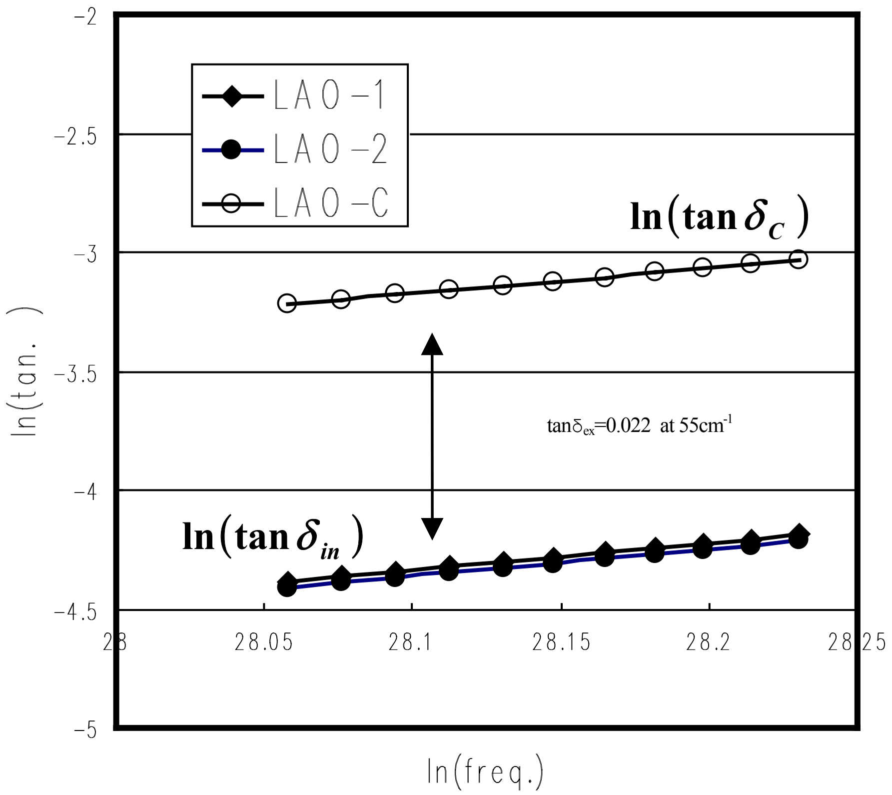

-4.15
-4.2
-4.25
-4.3
-4.35
-4.4
-4.45
28
28.05
28.1
28.15
28.2
28.25
ln(freq.)
ln(tan.)
$\ln(\tan\delta) = 1.130 \ln f + 36.08$
$\ln(\tan\delta) = 1.134 \ln f + 36.21$
LAO-1
LAO-2

Fig. 7



measured
fit
Reflectivity
wave number (cm⁻¹)
1.2
1
0.8
0.6
0.4
0.2
0
0
200
400
600
800
1000

Fig. 8



LAO-1
LAO-2
LAO-C
ln(tan δc)
tanδex=0.022 at 55cm-1
ln(tan δin)
ln(tan.)
ln(freq.)
-2
-2.5
-3
-3.5
-4
-4.5
-5
28
28.05
28.1
28.15
28.2
28.25