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Dielectric properties and far infrared reflectivity of lanthanum aluminate–strontium titanate ceramics

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Abstract

$LaAlO_3$–$SrTiO_3$ [$(1-x)$ LAO–xSTO] ceramics were prepared by a conventional solid-phase reaction method using high-purity reagents. Far infrared reflectivity spectra for $(1-x)$ LAO–xSTO ceramics were measured and eigenfrequencies and damping constants of the transverse and longitudinal optical modes were estimated in order to analyze the dielectric properties and lattice vibration parameters. The observed reflectivity spectra were fitted by 4 or 6 IR active modes in order to estimate the vibration eigenfrequencies and damping constants. In the range of microwave frequency, the permittivity and temperature coefficient of resonant frequency gradually increased with the amount of STO. The permittivity increase was due to increase in number of vibration mode by STO addition. The $Q\times f$ value of the solid solution showed the maximum value at $x=0.2$. The lattice vibrational analysis of the $(1-x)$ LAO–xSTO and the dielectric properties measured at the microwave frequency range indicate that the variation of $Q\times f$ value is related to the change in loss spectrum at the lower far infrared frequency with the amount of STO.

Keywords: Dielectric properties; Perovskites; Far infrared reflectivity

1. Introduction

Microwave dielectrics ceramics having permittivity of 37–45 are of current technological interest as dielectric filter materials in base station, especially dielectric resonator using low loss material in the $LnAlO_3$–$CaTiO_3$ or $LnAlO_3$–$SrTiO_3$ system, where the Ln abbreviates for lanthanide metals. These systems are drawing designers' attention for the microwave devices used in CDMA base station. Dielectric properties and sintering behavior of these ceramics were investigated by Moon et al.[1] They reported that $0.65LaAlO_3$–$0.35CaTiO_3$ ceramics have $\varepsilon_r=37$, $Q\times f=47000$ GHz and $\tau_f=5$ ppm/°C. Zheng et al.[2] investigated the variation of the crystal structure and dielectric properties of $NdAlO_3$–$CaTiO_3$ system as a function of the composition. Early investigation of this material was carried out by Jancar et al.[3] Their study was the earliest and detail investigation. Recently, Nenasheva[4] reported the microwave dielectric properties in $LnMO_3$–$CaTiO_3$ system. It is known that $LnAlO_3$–$SrTiO_3$ system has superior $Q\times f$ value as compared to that of $LnAlO_3$–$CaTiO_3$ system.[5] This led to the attention of many researchers in this system.[6] $LaAlO_3$ (LAO) shows relatively low dielectric loss but its temperature coefficient of resonant frequency (τ_f) is a large negative value.[7] The $SrTiO_3$ (STO), which shows large positive τ_f, is doped in to the LAO to improve the τ_f value.[8] This material was developed by Kyocera Corporation,[4] and it was reported that LAO and STO form a complete solid solution. However, the details of the dielectric properties for the complete range of compositions were not investigated. In the present study, dielectric properties of $(1-x)$ LAO–xSTO series, where $x=0$–0.7, and far infrared reflectivity of this solid solution in the range of $x=0$–0.3 were investigated. The dielectric losses obtained from infrared spectra were compared with that measured by microwave method.

2. Experimental procedure

The $(1-x)$ LAO–xSTO was prepared by the conventional mixed-oxide technique using high-purity oxides of lanthanum, aluminum and titanium (more than 99.9 mol%, lanthanum oxide was dried at 500 °C just before the weighing the chemical) and carbonate of strontium (dried powder has purity of 99.9 mol%). Stoichiometric quantities of these oxides and carbonate were mixed using distilled water as the mixing medium in a ball mill pot, and calcined for 4 h at 1400 °C. It was then pressed into cylindrical pellets at a pressure of 150 MPa and then sintered in the temperature range of 1580–1680 °C.

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The crystalline phases of the sintered ceramics were identified by X-ray diffraction method and it was confirmed that no second phases were present in the samples. The dielectric properties of all samples were evaluated by Hakki and Coleman's[9] open resonator method in the microwave range, using a network analyzer (HP8720D). The surfaces of the samples were wet polished using a 1 μm diamond slurry until the surface roughness (Ra) was less than 10×10^{-3} μm, and then washed with acetone in an ultrasonic bath to remove the particulate debris, which influence the IR reflection because of the scattering by the debris on the surface. Far infrared reflection spectra for the polished samples were collected at 25 °C with an FT-IR spectrometer (FT-IR; Bruker IFS-66V/S) having a SiC glow bar lamp. A gold reflector was used as the measurement reference. The measurements were carried out in vacuum system in order to avoid the influence of infrared absorption by water vapor. The incident angle of radiation was 11° and the spectral resolution was $1.0\,cm^{-1}$. The frequencies of lattice vibration were estimated by spectrum fitting.

3. Results and discussion

Figs. 1 and 2 show the variation of permittivity and $Q \times f$ value, respectively, with increasing STO content. As shown in these figures, permittivity gradually increased with amount of STO, whereas $Q \times f$ value showed a non-linear variation. The $Q \times f$ initially increased up to $x = 0.2$, after that it gradually decreased until $x = 0.7$. The permittivity was found to be sintering temperature independent and also, no temperature dependence of $Q \times f$ value was observed. Apparently, there is a maximum value of $Q \times f$ at a relatively small amount of STO. Fig. 3 shows the XRD patterns of $(1-x)$ LAO–xSTO system. There are no secondary phases in the ceramic matrix. In short, the variation of the $Q \times f$ value is not essentially due to secondary phases or impurities in the bulk material. Fig. 4 shows temperature coefficient of the resonant frequency (τ_f) of the $(1-x)$ LAO–xSTO ceramics. The τ_f curve indicated a parabolic increase with increasing STO content. The above-mentioned variations in the permittivity and τ_f can be easily predicted from the dielectric properties of LAO and STO. However, it is difficult to predict the variation of the $Q \times f$ values as gathered from Fig. 2. The measured far infrared reflectivity of the $(1-x)$ LAO–xSTO ($x = 0$, 0.1, 0.2 and 0.3) indicates that these variations can be attributed change in the lattice vibrations of $(1-x)$ LAO–xSTO.

The far infrared reflectivity obtained by FT-IR measurement of the $(1-x)$ LAO–xSTO are shown in Fig. 5a–d. Spectral fitting

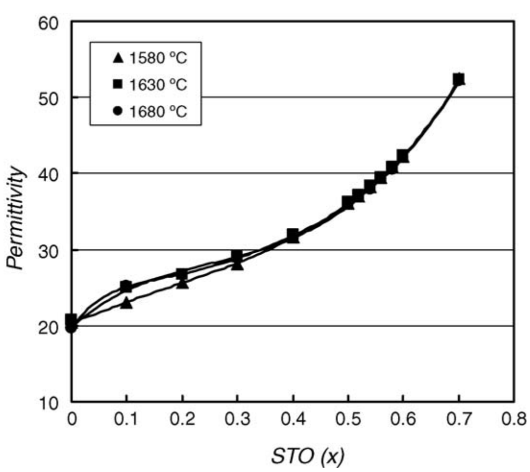

Fig. 1. Variation in permittivity of $(1-x)$ LAO–xSTO at microwave frequency.

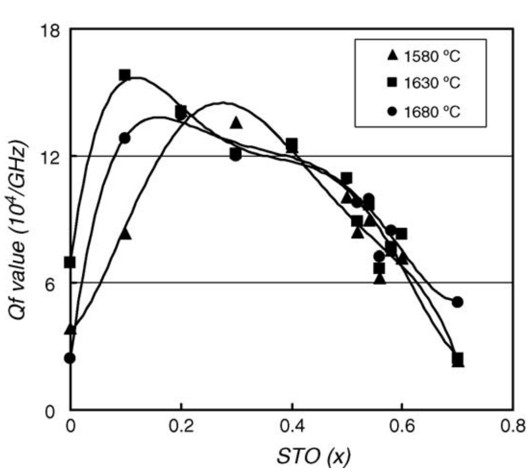

Fig. 2. Variation in $Q \times f$ value of $(1-x)$ LAO–xSTO at microwave frequency.

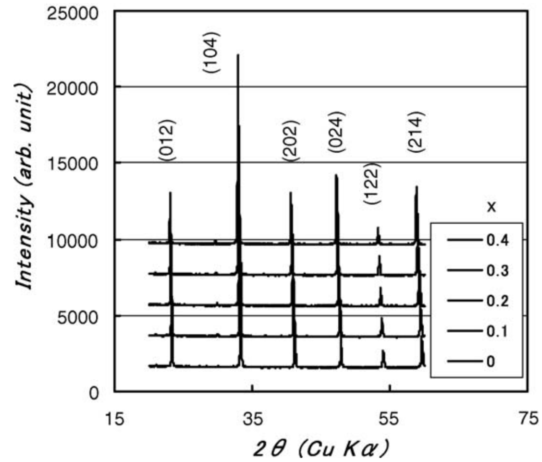

Fig. 3. XRD pattern of $(1-x)$ LAO–xSTO system.

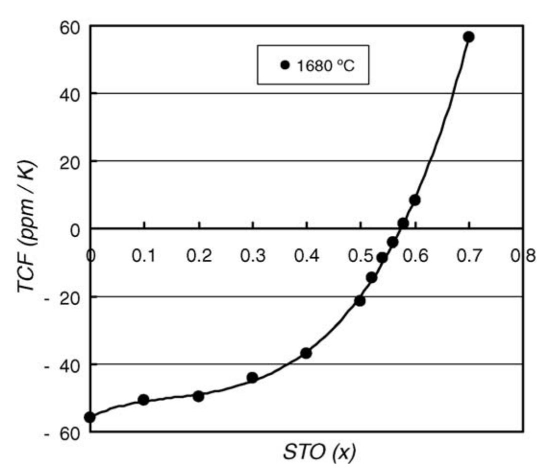

Fig. 4. Variation in τ_f value of $(1-x)$ LAO–xSTO at microwave frequency.

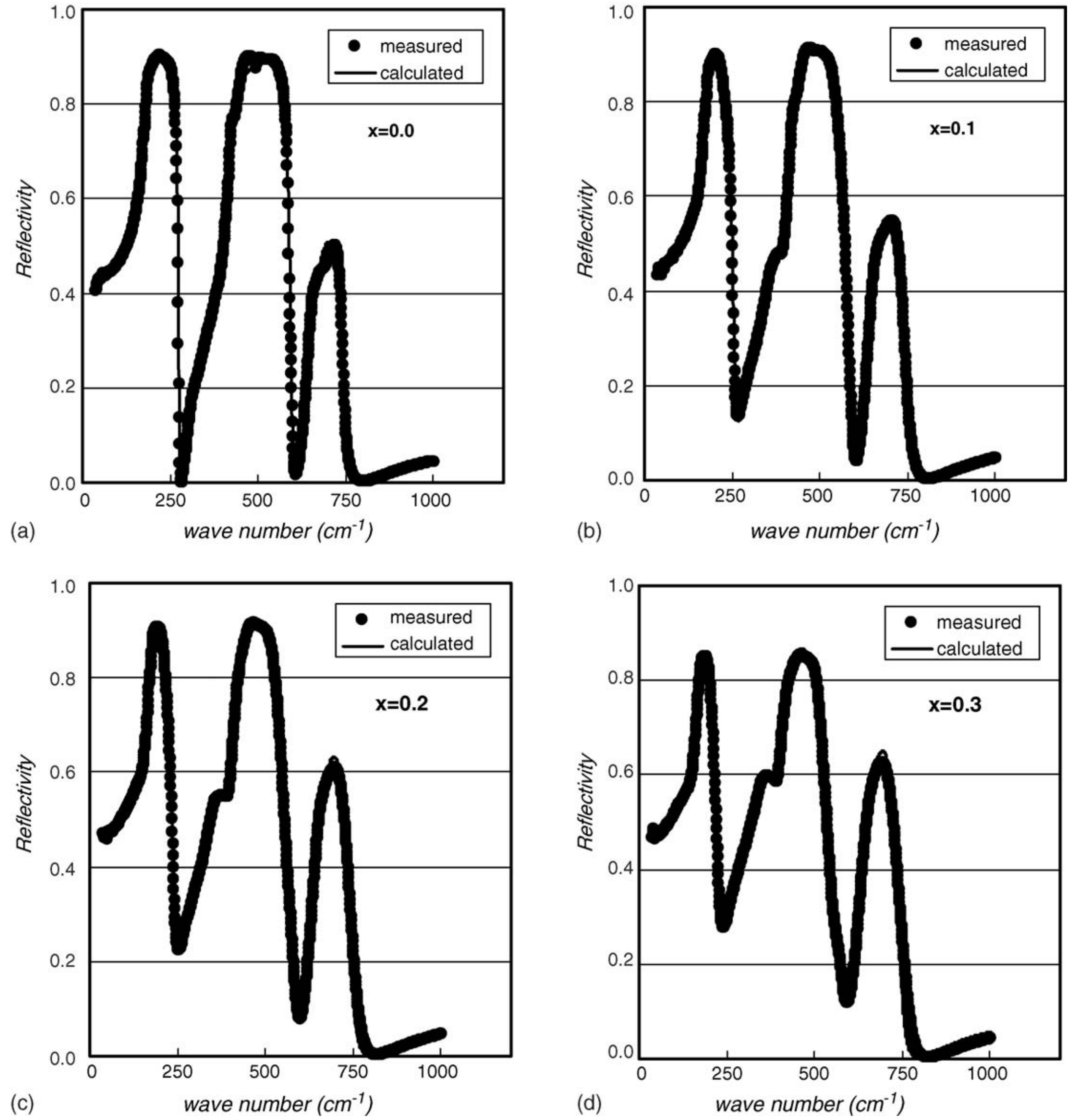

Fig. 5. Far IR reflectivity of $(1-x)$ LAO–xSTO. (a) $x=0$, (b) $x=0.1$, (c) $x=0.2$ and (d) $x=0.3$.

was carried out using permittivity dispersion relation (1) known as product rule.[10]

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

The normal modes at the center of Brillouin zone is classified from factor group analysis of the LAO as

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

Eq. (2) indicates 4 IR active modes in LAO.[11] However, since the symmetry of the LAO is varied by the STO addition, it is expected that new mode appeared in the spectrum by the variation of crystal symmetry. Fig. 5 shows the far infrared reflectivity of the LAO and $(1-x)$ LAO–xSTO, and as expected, two new modes appeared at 125 and 365 cm^{-1}. In order to investigate the relation between their new modes and the dielectric loss, the reflectivity was converted into loss spectrum of each lower frequency mode. Fig. 6 indicates the loss spectra of LAO and 0.8LAO–0.2STO solid solution. As shown in these loss spectra, it was apparent that the loss of the solid solution was lower than that of LAO in the low frequency range. Fig. 7 shows variation of the damping constants of the predominant mode (the lowest mode of the LAO) at near 180 cm^{-1} and the new mode (appeared in the solid solution). As shown in Fig. 7, it was considered that the decrease in loss factor with STO addition was brought about by decrease in damping constant of the predominant mode. The damping constant of the predominant mode decreased until $x=0.2$. After that, its value tends to increase with STO addition, so that the loss of the predominant mode at the low frequency shows a tendency to increase. In addition, vibration strength of the new mode became increased, hence it was considered that the loss of the new mode influenced total loss of the $(1-x)$ LAO–xSTO more than $x=0.3$. It was inferred that

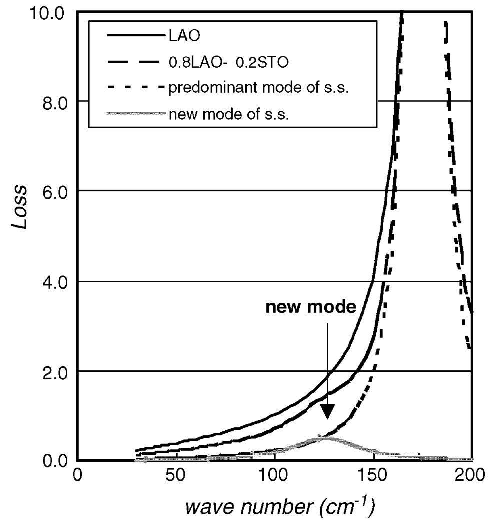

Fig. 6. Loss spectra of LAO and 0.8LAO–0.2STO solid solution at low IR frequency.

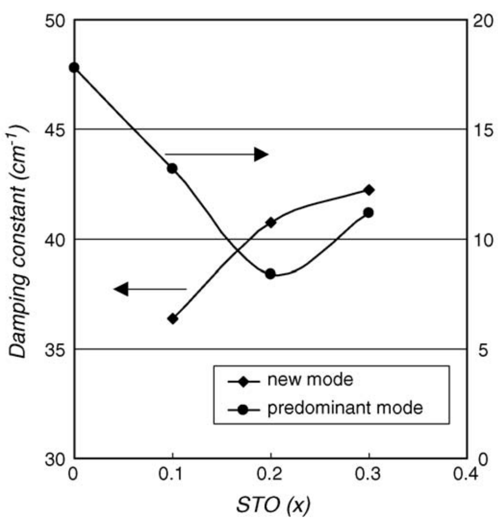

Fig. 7. Variation in the damping constant of the predominant mode and new mode.

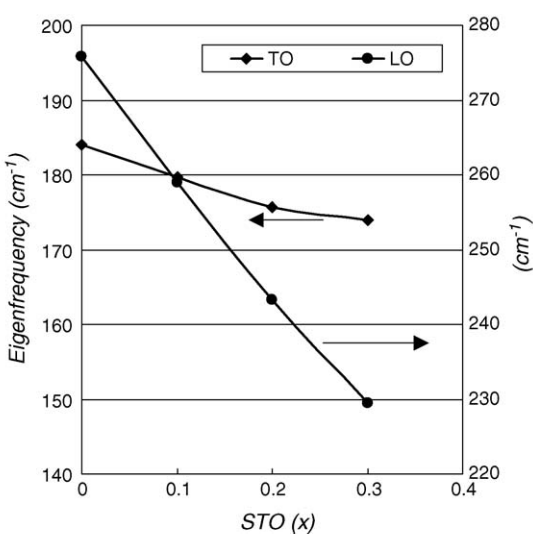

Fig. 8. Variation in LO and TO eigenfrequency of the predominant mode.

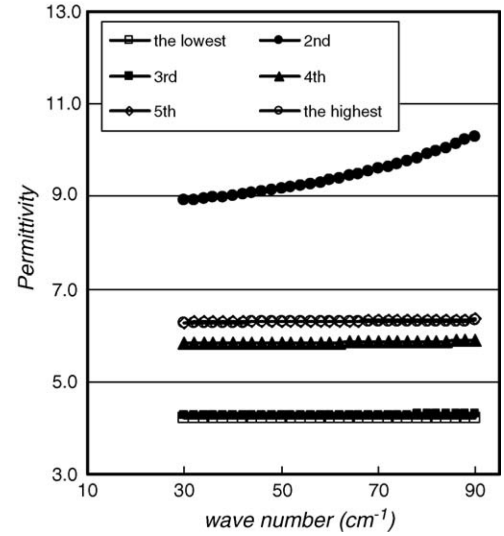

Fig. 9. Comparison with each vibration mode in 0.9LAO–0.1STO.

the above-mentioned variation of the lattice vibration brought about the change in the microwave dielectric loss ($Q \times f$ value). Fig. 8 shows the variation of the optical mode's frequencies in the predominant vibration. The difference between LO and TO frequencies decrease with STO addition. This decrease means decrease in vibration strength in the predominant mode, namely it indicates the decrease in low-frequency permittivity. However, as shown in Fig. 9, permittivity of all modes in the $(1-x)$ LAO–xSTO contributes to total permittivity. Therefore, it is considered that the increase in the permittivity by STO addition in the $(1-x)$ LAO–xSTO system is caused by change in number of vibration mode from 4 to 6.

4. Conclusions

In the present study, the variation of the dielectric properties of $(1-x)$ LAO–xSTO system was investigated and the following results for the relation between the dielectric properties and lattice vibration were obtained. (a) The unique variation of $Q \times f$ value at microwave frequency are related to the change in loss spectrum with amount of STO. (b) The increase in permittivity is due to increase in number of the vibration mode.

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