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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

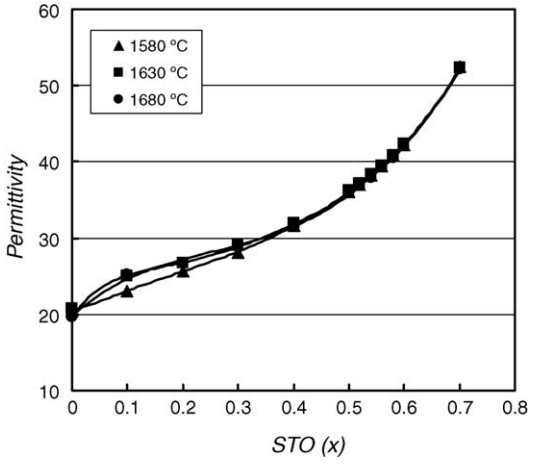

Fig. 1. Variation in permittivity of $(1 - x)$ LAO–xSTO at microwave frequency.

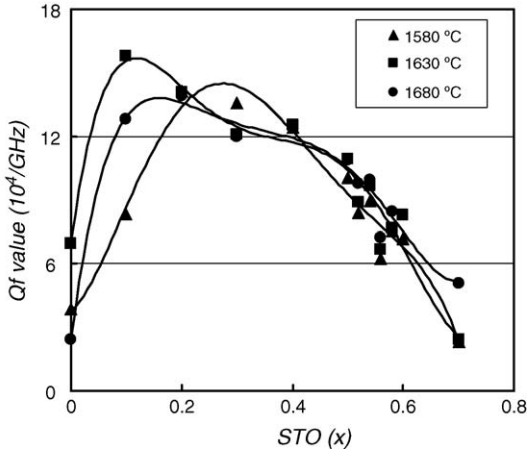

Fig. 2. Variation in $Q \times f$ value of $(1 - x)$ LAO–xSTO at microwave frequency.

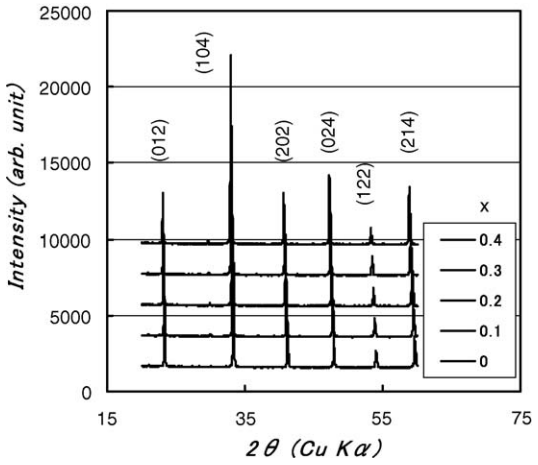

Fig. 3. XRD pattern of $(1 - x)$ LAO–xSTO system.

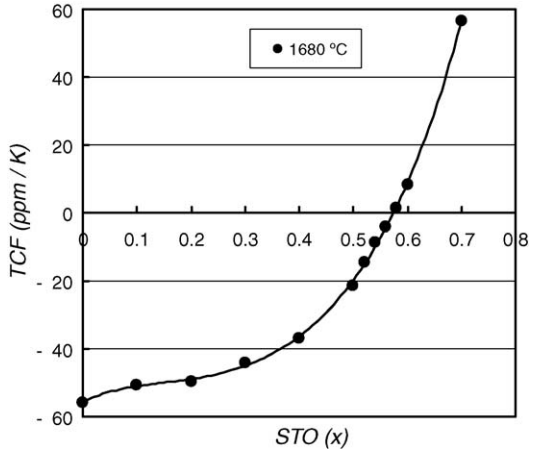

Fig. 4. Variation in τ_f value of $(1 - x)$ LAO–xSTO at microwave frequency.