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Far-infrared reflection of $(Sr_{1-x},Ca_x)(Ga_{1/2},Ta_{1/2})O_3$ ceramics

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Abstract

Far-infra-red reflectivity for $Sr(Ga_{1/2},Ta_{1/2})O_3$ and $(Sr_{1-x},Ca_x)(Ga_{1/2},Ta_{1/2})O_3$ ceramics was observed and effective charges of the ions in their ceramics were calculated in order to investigate the relationship between the effective charges and the dielectric properties in the range of microwave frequencies. These ceramics were prepared by conventional solid phase reaction using high purity reagents. The observed reflectivity spectra were fitted using four infra-red (IR) active modes predicted by factor group analysis in order to estimate the vibration frequencies. The effective charges were calculated from the mode frequencies and the lattice constants. The relationship between the effective charges and Qf values was discussed to find the causes of dielectric loss of $(Sr_{1-x},Ca_x)(Ga_{1/2},Ta_{1/2})O_3$ ceramics.

Keywords: Applications; Compositions; Dielectric properties; Fuctional applications; Perovskites; Properties

1. Introduction

$Ba(Zn_{1/3},Ta_{2/3})O_3$; BZT ceramic shows great and interesting properties at microwave frequency. Kageyama et al., prepared $Sr(Ga_{1/2},Ta_{1/2})O_3$; SGT as the special additive for BZT ceramics and reported the great dielectric properties of BZT–SGT solid solution.[1] Many workers have improved the dielectric properties of BZT, but the fundamental properties of SGT have hardly been investigated. So far we have investigated and reported on characteristics and properties of SGT, $(Sr_{4/5},Ca_{1/5})(Ga_{1/2},Ta_{1/2})O_3$; SCGT-1 and $(Sr_{3/5},Ca_{2/5})(Ga_{1/2},Ta_{1/2})O_3$; SCGT-2, and discussed the effect of the additive material for BZT.[1,2] Recently we started to study the relationship between dielectric properties and lattice vibration of SGT, SCGT-1 and SCGT-2. In general, the complex perovskite ceramics are the ionic polycrystals, so that the dielectric properties at microwave frequencies could be characterized by the ionic polarization, it can be analyzed by observation of the far-infrared reflection. Sagala and Fukuda tried to apply the four parameter semi quantum (FPSQ) model proposed by Gervais et al.[3] instead of the classical dispersion theory in order to obtain the lattice vibration frequencies of $Ba(Mg_{1/3},Ta_{2/3})O_3$ and $Ba(Mg_{1/3},Nb_{2/3})O_3$.[4,5] Nakagawa reported the analysis of lattice vibration of the perovskite type fluorides.[6] In his report, the frequencies of transverse and longitudinal optical modes (TO and LO respectively) estimated from the infrared spectra were applied to a rigid ion model and the effective ion charges were calculated from them. Investigation of effective charges of some ions in $A(B'_{1/2},B''_{1/2})O_3$; A = Ba were carried out by Zurmühlen et al.[7] They observed the far-infrared reflectivity of some ceramics and calculated the effective charges from the dispersion parameters. No clear relationship between the effective charges and the dielectric losses was found in their conclusion.

In the present study, the far-infra-red spectra fittings of SGT and $(Sr_{1-x},Ca_x)(Ga_{1/2},Ta_{1/2})O_3$; SCGT were carried out with high accuracy by using the FPQS model. Then, the effective charges of the ions in their ceramics were calculated in order to survey the relationship between the effective charges and dielectric properties.

1.1. Experimental procedure

SGT and two kinds of SCGT were prepared by the conventional mixed-oxide reaction method. Gallium and tantalum oxides and calcium and strontium carbonates used to prepare SGT and SCGT were of high purity grade reagent (more than 99.9 mass%). These oxides and carbonates were mixed by ball mill and calcined for 2 h at 1200 °C, then sintering was carried out at temperatures between 1400 and 1650 °C after pressing. It was confirmed by X-ray diffraction analysis that no second phases were formed in SGT, SCGT-1 and SCGT-2 matrices.

The surfaces of the samples were wet polished using about 1 μm diamond slurry by which the surface

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roughness (Ra) was less than 5×10^{-3} μm, and then washed with acetone in an ultrasonic bath to remove the influence of impurities into infra-red (IR) measurement. Dielectric properties of their ceramics were measured by Hakki and Coleman's open resonator method at microwave range. Far-infra-red reflection spectra of the samples were measured at 25 °C with a Fourier Transform Infrared Spectroscopy (FT–IR) spectrometer having a SiC glow bar lamp. Au reflector was used as the measurement reference. The incident angle of radiation was 11° and the spectra resolution was 1.0 cm^{-1}. The frequencies of lattice vibration were estimated by spectrum fitting.

2. Results and discussion

Fig. 1 shows X-ray diffraction patterns of SGT, SCGT-1 and SCGT-2. Lattice constants of each material refined by Rietveld fitting are listed with R factors in Table 1. The Rietveld analysis showed that these ceramics were of a complex perovskite structure represented by space group Fm3m(O_h^5). The ion configuration in SGT and SCGT obtained from the Rietveld analysis is illustrated in Fig. 2. The occupation ratio of Ga and Ta ions in the B sites (B_1' and B_1'') are summarized in Table 2, and the B sites (B_2' and B_2'') in the neighboring plane are occupied in the opposite ratio of Ga and Ta ions.

Permittivity and Qf values of SGT and SCGT measured by Hakki and Coleman's method at microwave frequencies are shown in Fig. 3. It shows that the permittivity increases with Ca substitution up to $x=0.2$ and then it decreases gradually, while Qf value rapidly decreases with Ca substitution and reaches a bottom at $x=0.2$. After that Qf value increases steadily to about 50 000 GHz. This tendency of Qf value could be also distinguished in $(Sr_{1-x},Ba_x)(Ga_{1/2},Ta_{1/2})O_3$.[8]

Such a sudden change of Qf value as observed around $x=0.2$ might be brought about by ionicity change of the ions in SGT and SCGT. IR reflectivity spectrum provides the information concerned with the ionic state. Reflectivity spectra of SGT, SCGT-1 and SCGT-2, in which samples a significant change of Qf value was observed, are shown by black circles in Fig. 4 (a)–(c). For the crystal structure represented by space group O_h^5, the following irreducible representation is derived by the factor group analysis for the Brillouin-zone-center vibrational modes.[7]

$$\Gamma = A_{1g} + E_g + F_{1g} + 5F_{1u} + 2F_{2g} + F_{2u} \quad (1)$$

This representation shows five F_{1u} modes, but the secular equation of the lattice vibration matrix gives one acoustic mode, therefore the representation Eq. (1) predicts only four IR active modes at Γ point. The calculated reflectivity spectra of SGT, SCGT-1 and SCGT-2 obtained by spectra fitting are shown by solid lines in Fig. 4(a)–(c). It was assumed in the calculation that IR active vibrations were four modes. Permittivity was calculated from Eq. (2), which is well-known as a dispersion relation derived from the FPQS model.

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

Table 1
Results of Rietveld analysis and dielectric properties

Materials	Lattice constant (Å)	R.wp	R.p	R.e	Space
SGT	7.8930	8.74	6.65	5.82	Fm3m
SCGT-1	7.8685	9.64	8.32	4.39	Fm3m
SCGT-2	7.8378	10.08	9.12	4.57	Fm3m

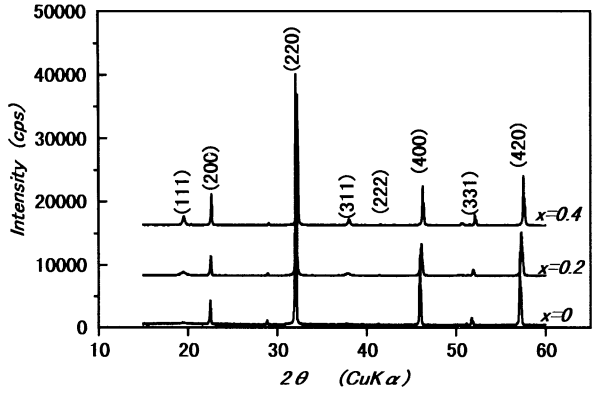

Fig. 1. X-ray diffraction patterns of SGT, SCGT-1 and SCGT-2.

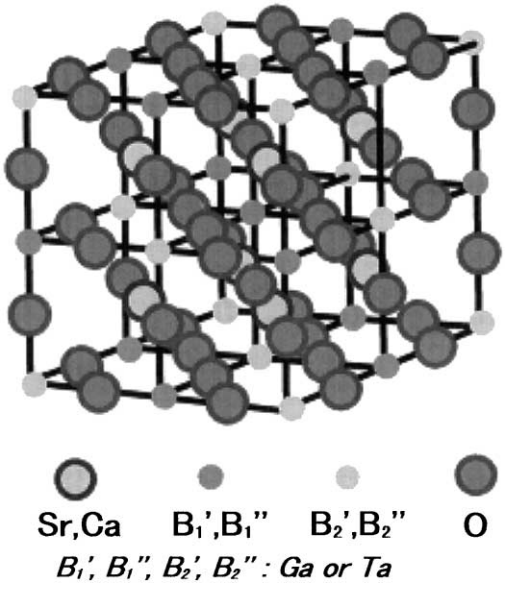

Fig. 2. Crystal structure of SGT and SCGT.

Table 2
Occupation factors of Ta and Ga ions in B_1' and B_1'' sites

	SGT	SCGT-1	SCGT-2
Ga in B_1' site	0.3747	0.2816	0.1364
Ta in B_1'' site	0.6253	0.7184	0.8636

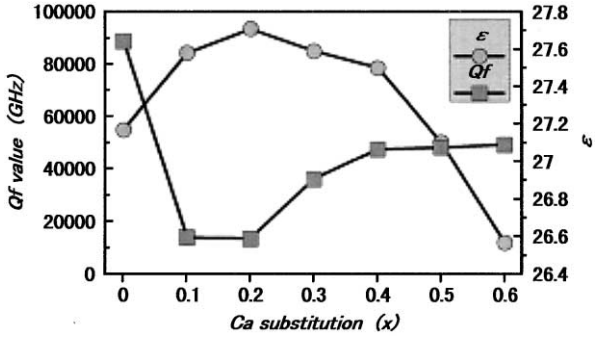

Fig. 3. Dielectric properties of SGT and SCGT.

The permittivity were transformed into reflectivity by a following relation.[3]

$$R = \left|\varepsilon^{1/2} - 1\right| / \left|\varepsilon^{1/2} + 1\right| \tag{3}$$

where ε, R, ε_∞ and ω are the permittivity, the reflectivity, the permittivity at high frequency and the frequency, respectively. $\Omega_{j\mathrm{LO}}$ and $\Omega_{j\mathrm{TO}}$ are the eigen frequencies of LO and TO modes, and $\gamma_{j\mathrm{LO}}$ and $\gamma_{j\mathrm{TO}}$ are the damping constants of LO and TO modes, respectively. As shown in Fig. 4(a)–(c), the calculated curves are in good agreement with the measured ones and the obtained vibration frequencies and damping constants are listed in Table 3. Permittivity extrapolated to $\omega = 0$; ε_0, and ε_∞ are also listed in Table 3. Then, in order to consider the relationship between Qf values and the ionicity of the material constituents, the effective charges of the ions were estimated from the LO and TO frequencies listed in Table 3. According to the relationship derived by Born and Huang,[9] the frequency difference is expressed by

$$\sum_{j=1}\lambda_{Lj} - \sum_{j=1}\lambda_{Tj} = Tr\left[F^c_{\mathrm{LO}} - F^c_{\mathrm{TO}}\right]. \tag{4}$$

Where F^c_{LO} and F^c_{TO} are long range Coulomb potential matrices for LO and TO modes.

However, it should be noted that Eq. (4) includes the assumption that the ions act as the core shells in the crystal.

In the center of Bullouin-zone, Eq. (4) is transformed to Eq. (5).

$$\sum_{j=1}\lambda_{Lj} - \sum_{j=1}\lambda_{Tj} = \frac{4\pi e^2}{V}\beta \tag{5}$$

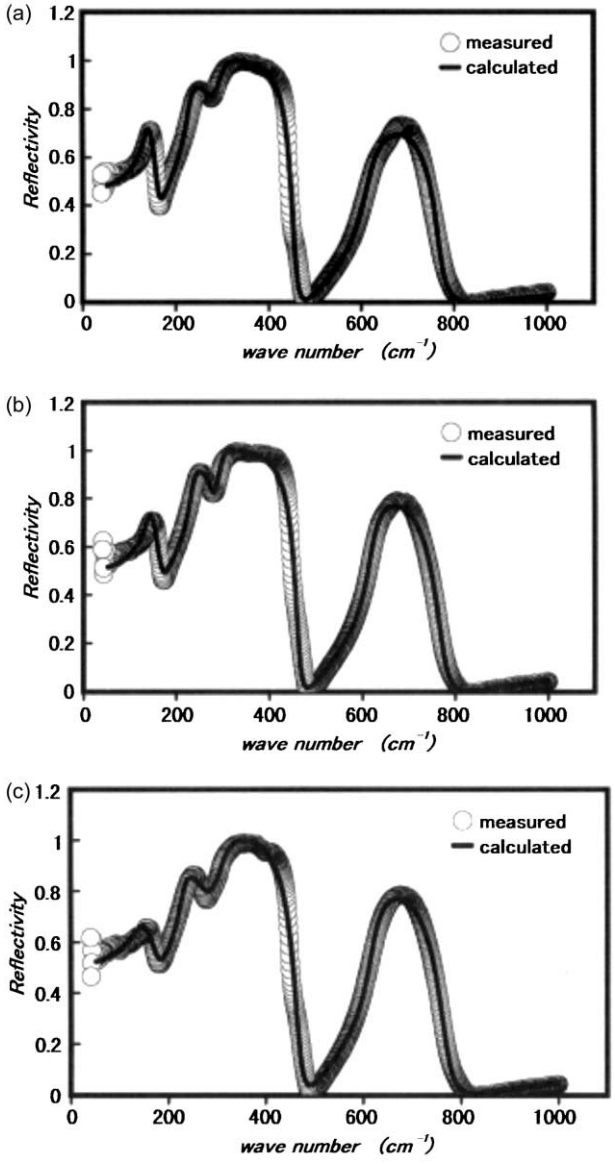

Fig. 4. IR reflectivity of SGT, SCGT-1 and SCGT-2. (a) SGT ($x = 0$); (b) SCGT-1 ($x = 0.2$); (c) SCGT-2 ($x = 0.4$).

where,

$$\beta = \sum_{i=1} k_i \frac{Z_i^2}{m_i},\ \lambda_{Lj} = 4\pi^2\Omega_{Lj}^2,\ \lambda_{Tj} = 4\pi^2\Omega_{Tj}^2 \tag{6}$$

V, e, Z_i, m_i, k_i, and Ω_j denote the volume of unit cell, the electron charge, the effective charge given in elementary electric charge, the mass of i species ion, the coefficient concerning the number of the ion i in unit cell and the eigen frequency of j-th mode given in cm^{-1} (see Ref. 9 for the general statement.).L and T denote the longitudinal and the transverse modes, respectively. The effective charges were calculated by the method of the least squares using Eq. (5). Results of the estimation are listed in Table 4, where ΣZ implies the total effective charges of the ions in the unit cell in Table 4. These data

Table 3
Frequencies and damping parameters of SGT, SCGT-1 and SCGT-2

j	SGT				SCGT-1				SCGT-2			
	$\varepsilon_0=28.5$, $\varepsilon_\infty=3.59$				$\varepsilon_0=34.0$, $\varepsilon_\infty=4.40$				$\varepsilon_0=35.4$, $\varepsilon_\infty=4.42$			
	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$	$\Omega_{j\mathrm{LO}}$	$\gamma_{j\mathrm{LO}}$	$\Omega_{j\mathrm{TO}}$	$\gamma_{j\mathrm{TO}}$
	(cm^{-1})											
1	161.3	24.9	138.2	17.1	164.9	31.4	141.6	18.5	176.0	45.6	147.6	38.5
2	286.1	45.3	230.9	15.5	283.0	31.1	234.9	12.4	289.2	78.0	232.2	17.4
3	555.1	16.0	291.2	33.4	462.2	17.9	289.5	21.3	468.3	27.1	303.5	44.8
4	766.0	27.5	613.5	42.4	769.7	31.7	620.0	28.9	768.4	36.0	618.6	31.8

Table 4
Effective charges of the ions in SGT, SCGT-1 and SCGT-2

Materials	Z_i					ΣZ_i
	Sr	Ca	Ga	Ta	O	
SGT	1.09		1.99	4.19	−1.40	8.46×10^{-8}
SCGT-1	1.01	1.01	1.92	4.41	−1.39	3.75×10^{-6}
SCGT-2	1.08	1.08	1.93	4.23	−1.39	1.00×10^{-6}

mean the variation of the bonding state of B site ion in BO_6 octahedra in SGT and SCGT. The effective charges show quite contrary variation to the dielectric loss, and it apparently seems a reasonable relationship between their properties. However, it is required to observe the agreement between the microwave permittivity and the low frequency limit of the fitted permittivity in order to conclude its relationship. Also high quality (and low temperature) measurement and fitting of the IR reflectivity at low frequency are required in order to obtain the lowest frequency damping. Therefore, we could not get to conclude the relationship between the microwave Qf value and the effective charge of Ta ion even though the bonding state in BO_6 octahedra was changed by Ca substitution. Further work is necessary to clear the effect of Ta ion charge into microwave dielectric properties.

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