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Structure evolution and microwave dielectric characteristics of Ca[($Al_xGa_{0.5-x}Nb_{0.5}$)$_{0.5}Ti_{0.5}$]O_3 ceramics

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ABSTRACT

The microwave dielectric characteristics of Ca[($Al_xGa_{0.5-x}Nb_{0.5}$)$_{0.5}Ti_{0.5}$]O_3 ($x = 0, 0.1, 0.2, 0.4, 0.5$) ceramics were investigated together with the structure evolution. Distorted perovskite structure in space group *Pbnm* with $b^-b^-c^+$ tilting was determined for the present solid solutions, where the microstructures were remarkably affected by Al-content. Owing to the Al-substitution which was accompanied by the subdued octahedral tilting, the *Qf* value reached up to 40,000 GHz with increasing *x*, the dielectric constant (ε_r) remained at around 50, and the temperature coefficient of resonant frequency (τ_f) could be adjusted to near zero. Low-loss temperature-stable microwave dielectric ceramics with medium dielectric constant were obtained at $x = 0.2–0.5$, which exhibited *Qf* values of 35,900–40,000 GHz, ε_r of 49.2–53.4, and τ_f of 0.6–3.5 ppm/°C.

1. Introduction

Complex perovskites constitute important subgroup of microwave dielectric ceramics in virtue of the excellent and tunable microwave dielectric properties [1,2]. Typical $Ba(B'_{1/3}B''_{2/3})O_3$ (B' = Zn, Mg, Co and Ni, B'' = Ta, Nb) complex perovskites which have been commercially applied in resonators and filters indicate the ultra-high *Qf* value, while the dielectric constant is usually below 40 [3–6]. With the rapid development of microwave communication towards high-band microwave and millimeter wave range, low loss microwave dielectric ceramics with higher dielectric constant ($\varepsilon_r = 45–70$) have received increasing attention in recent decades [7–17].

On the other hand, the temperature-stable dielectrics with medium dielectric constant have been extensively achieved by forming solid solution between $A(B'_{0.5}B''_{0.5})O_3$ complex perovskites (negative τ_f) and $CaTiO_3/SrTiO_3$ (positive τ_f), such as $0.5Ca(Al_{0.5}Nb_{0.5})O_3$-$0.5CaTiO_3$ (ε_r = 45.3, *Qf* = 29,600 GHz, τ_f = −1.0 ppm/°C) [7], $RE(Mg_{0.5}Ti_{0.5})O_3$-$SrTiO_3$ [8,12], and $RE(Zn_{0.5}Ti_{0.5})O_3$-$CaTiO_3$ (RE = La and Nd) [13]. However, compared with $Ba(B'_{1/3}B''_{2/3})O_3$ complex perovskites, whose dielectric characteristics are commonly referred to be dominated by the degree of 1:2 cation ordering and ordering domain structures [3–6,18], few systematic studies of $A(B'_{0.5}B''_{0.5})O_3$ complex perovskites that combine dielectric properties with *B*-site 1:1 ordering/disordering and octahedral tilting have been reported. In our previous work, low-loss, temperature-stable ceramics with medium dielectric constant have been obtained by forming solid solution between $A(Ga_{0.5}Nb_{0.5})O_3$ and $ATiO_3$ (*A* = Ca, Sr) [16,17]. Local 1:1 ordering between Ga^{3+} and Nb^{5+} is detected in $Sr(Ga_{0.5}Nb_{0.5})O_3$ ceramics while the ordered structure is disrupted by Ti^{4+} substitution in *B*-sites. The *Qf* value is affected by the ordering transition from long-range ordering to short-range ordering with Ti-substitution [16]. Nevertheless, distorted perovskite with octahedral tilting is determined for the solid solution between $Ca(Ga_{0.5}Nb_{0.5})O_3$ and $CaTiO_3$, while no *B*-site ordering is detected. Microwave dielectric characteristics of $Ca(Ga_{0.5}Nb_{0.5})O_3$-$CaTiO_3$ ceramics are considered to be relevant to the structure modification which contains oxygen octahedral tilting [17]. Though octahedral tilting is expected to affect perovskite structure and dielectric properties [17,19], systematic studies of octahedral tilting in $A(B'_{0.5}B''_{0.5})O_3$ complex perovskites correlated with its influence on microwave dielectric properties have rarely been reported.

Moreover, Al and Ga exhibit similar physical and chemical properties except that Ga has a tendency to volatilize at high temperature [17,20], resulting in lattice defect in perovskite structure, which increases the dielectric loss severely [21]. Therefore, the reduced dielectric loss is expected by Al-substitution for Ga in Ca

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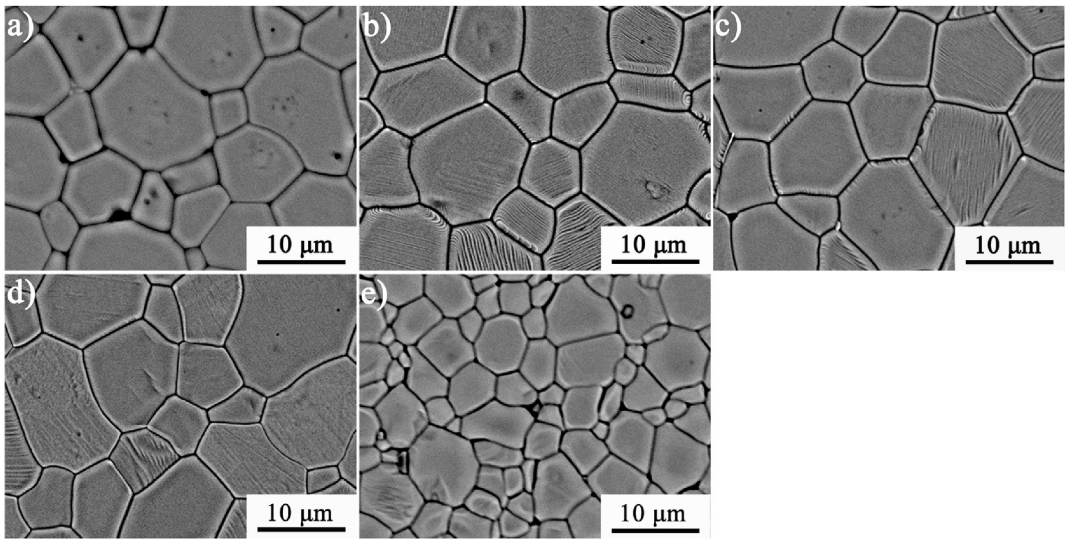

Fig. 1. BSE micrographs of thermally etched surfaces of $Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ ceramics: (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, sintered at 1425 °C for 3 h and thermally etched at 1375 °C for 30 min; (d) $x = 0.4$, sintered at 1450 °C for 3 h and thermally etched at 1400 °C for 30 min; (e) $x = 0.5$, sintered at 1525 °C for 3 h and thermally etched at 1475 °C for 30 min.

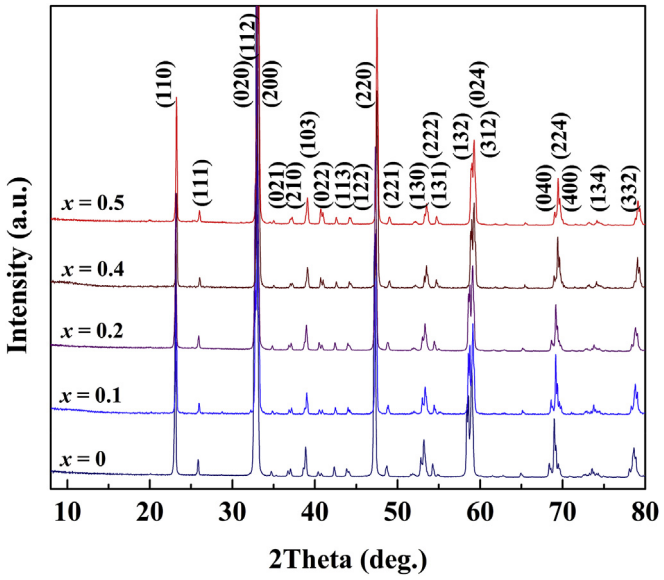

Fig. 2. Step scanning XRD patterns of $Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ ceramics. The samples for $x = 0$–0.2 are sintered at 1425 °C, the samples for $x = 0.4$ are sintered at 1450 °C, and those for $x = 0.5$ are sintered at 1525 °C.

$[(Ga_{0.5}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ ceramics (ε_r = 55.4, Qf = 31,000 GHz, τ_f = 14.0 ppm/°C) [17]. In addition, the raw material costs could be lowered by utilizing Al instead of expensive Ga. Besides, the ionic radius of Al^{3+} (0.535 Å) is smaller than that of Ga^{3+} (0.620 Å) [22]. Hence, the tolerance factor (t) of $Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ which is subject to the constituent ionic radius would increase as Al-substitution augments. Since the octahedral tilting characteristics depend on the value of t [23,24], the variation of the octahedral tilting with increasing x is supposed to affect the microwave dielectric properties of $Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ complex perovskites.

Considering the effects of modified octahedral tilting and suppressed Ga-volatilization, low loss dielectric ceramics with moderate dielectric constant ($\varepsilon_r \geq 50$) are expected by Al-substitution in $Ca[(Ga_{0.5}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$. Thus, in the present work, structure evolution and microwave dielectric characteristics of $Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ ceramics are investigated for an improved understanding of structure-property relations in $A(B'_{0.5}B''_{0.5})O_3$ complex perovskites.

2. Experimental procedure

$Ca[(Al_xGa_{0.5-x}Nb_{0.5})_{0.5}Ti_{0.5}]O_3$ (x = 0, 0.1, 0.2, 0.4, 0.5) ceramics were prepared via the standard solid-state sintering method from high-purity powders of $CaCO_3$ (99.99%), Al_2O_3 (99.99%), Ga_2O_3 (99.9%), Nb_2O_5 (99.99%), and TiO_2 (99.99%). Stoichiometric quantities of raw materials were weighed and mixed by ball milling with yttrium-stabilized zirconia media in ethanol for 24 h. After drying, the mixtures were calcined at 1250 °C in air for 3 h. The calcined powers with 6 *wt%* of PVA (polyvinyl alcohol) solution were pressed into disks under the pressure of 98 MPa with 12 mm in diameter and 2–6 mm in height. The disks were sintered at 1350 °C-1550 °C in air for 3 h. After cooling from the sintering temperature to 800 °C at a rate of 2 °C/min, the ceramics were further cooled naturally inside the furnace.

The crystal structures of sintered samples were identified by X-ray powder diffraction analysis with Cu$K\alpha$ radiation (RIGAKU D/max 2550PC; Rigaku Co., Tokyo, Japan). The step-scanning XRD data were collected over the range of $2\theta = 8°$-130°, with a step size of 0.02° and a count time of 2 s. The Rietveld structure refinements were carried out with the FULLPROF program [25]. The grain morphology of ceramics was evaluated on polished and thermal etched surfaces by scanning electron microscopy (SEM) equipped with the back-scattered electron (BSE) attachment (S-3700N, Hitachi, Tokyo, Japan), at which mode the possible existence of second phase can be detected. The ceramics for x = 0–0.2, x = 0.4 and x = 0.5 were sintered at 1425 °C, 1450 °C and 1525 °C, respectively. Thus the samples for x = 0–0.2, x = 0.4 and x = 0.5 were thermally etched at 1375 °C, 1400 °C and 1475 °C for 30 min, respectively. Samples for transmission electron microscopy (TEM) analysis were prepared by disaggregating the ceramics and then grinding in an agate mortar. Finally, the powders were suspended in alcohol and then dispersed onto a carbon-coated copper grid. The selected area electron diffraction (SAED) patterns and high-resolution TEM (HRTEM) images were obtained by transmission