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Microwave dielectric properties of ZrO_2 and SnO_2 doped $Ca_5Nb_4TiO_{17}$ ceramics

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ABSTRACT

In this study, the effects of B-site dopants, such as Sn^{4+} and Zr^{4+} ions, on the microwave dielectric properties of the $Ca_5Nb_4TiO_{17}$ ceramic were investigated, in contrast to the replacement of A-site ions shown in literature. The sintering temperature of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramics depended on the Sn^{4+} content, while the Zr^{4+} dopant had no impact on the densification of the $Ca_5Nb_4Ti_{1-x}ZrxO_{17}$ ceramics. Both the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ and $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ samples have a dense microstructure with closely packed plate-like grains and little porosity. The relative permittivity ε_r of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramics decreased from 45.0 for $x = 0$ to 30.3 for $x = 1.0$, because the more highly polarizable TiO_2 ($\alpha = 15.6$ Å^3) was replaced by the less polarizable SnO_2 ($\alpha = 6.70$ Å^3). The quality factor ($Q \times f$) value increased significantly to 33,542 GHz for $x = 0.3$, which was primarily caused by the increase in the average grain size. The temperature coefficient of resonance frequency (τ_f) of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramics moved toward the positive direction with the Sn^{4+} substitution. The ε_r value of the $Ca_5Nb_4Ti_{1-x}ZrxO_{17}$ ceramics decreased almost linearly from 45.2 for $x = 0$ to 40.6 for $x = 0.5$ with an increase in Zr^{4+} content, due to the lower molecular polarizability of ZrO_2 ($\alpha = 7.33$ Å^3). The $Q \times f$ and τ_f values were observed to decrease with an increasing x value, which can be explained by the decreasing degree of ordering.

1. Introduction

Dielectric ceramics with the general formula $A_nB_nO_{3n+2}$ (A = Ca, Sr, Mg, or La; B = Ti or Nb) have drawn considerable interest since they possess a combination of important piezoelectric, ferroelectric, and electrical properties [1,2]. Their crystal structures are derived from the ABO_3 perovskite-type layer structure with slabs of corner-shared BO_6 octahedra separated by an interslab region [3–5]. The crystal structure type is given by the n value, which is the number of octahedral layers in the perovskite slab, and can be tuned by tailoring the oxygen content. Generally the $n = 4$ members of the $A_nB_nO_{3n+2}$ compounds, such as $La_2Ti_2O_7$ and $Sr_2Nb_2O_7$, are ferroelectric at room temperature with super-high Curie points, and are used as high-temperature piezoelectrics [4]. Recently, compositions with $n = 5$ and 4.5 members, such as $(CaLa_4)Ti_5O_{17}$ and $(Ca_{0.5}La_4)Ti_{4.5}O_{15.5}$ (i.e., $CaLa_8Ti_9O_{31}$), were found to be paraelectrics with low dielectric loss and high thermal stability, suggesting great potential application in microwave dielectrics [3,4,6,7].

More recently, several $n = 5$ members in the $A_5B_5O_{17}$ series, including $Ca_5Ta_4TiO_{17}$, $Ca_5La_4TiO_{17}$, and $Ca_5Nb_4TiO_{17}$ ceramics, have been shown to possess good microwave dielectric properties. Jawahar et al. presented the microwave dielectric properties of $Ca_5La_4TiO_{17}$ ceramic, including $\varepsilon_r = 55.2$, $Q \times f = 17{,}359$ GHz, and $\tau_f = -20$ ppm/°C [8], and Joseph et al. reported that $Ca_5Nb_4TiO_{17}$ and $Ca_5Ta_4TiO_{17}$ ceramics possessed an ε_r of 44.9 and 40.1, respectively, a $Q \times f$ of 17,600 and 16,450 GHz, respectively, and a τ_f of approximately −112.9 and −53.6 ppm/°C, respectively [9]. Two modifications were reported for the room-temperature structure of the $Ca_5Nb_4TiO_{17}$ ceramic, including one with the polar symmetry P2m, and another with the non-polar symmetry $P2_1/c$ [3,4,10]. Besides the contradictory report on the crystal structure, to the best of our knowledge, reports in the literature regarding the effects of the dopants on the microwave dielectric properties of the $Ca_5Nb_4TiO_{17}$ ceramic were very limited. Anjana et al. reported that partial substitution of the Ca^{2+} ions with Mg^{2+} ions in a $Ca_5Nb_4TiO_{17}$ ceramic was found to lower its sintering temperature and resulted in the microwave dielectric properties of an ε_r of 37.5, a $Q \times f$ of 22,500 GHz, and a τ_f of approximately −4.3 ppm/°C [11]. On

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the other hand, Li et al. showed that the microwave properties of $Ca_{4.6}Zn_{0.4}Nb_4TiO_{17}$ exhibited $\varepsilon_r = 52$, $Q \times f = 9937$ GHz, and $\tau_f = -8.6$ ppm/°C [12], while Manan et al. reported that the ε_r, $Q \times f$, and τ_f values of the $Ca_3Sr_2Nb_4TiO_{17}$ ceramic were 53.4, 1166 GHz, and −6.5 ppm/°C, respectively [6].

In contrast to the replacement of A-site ions shown in literature, the objective of this study was to investigate the effects of B-site dopants such as Sn^{4+} and Zr^{4+} ions on the densification, microstructural evolution, and microwave dielectric properties of the $Ca_5Nb_4TiO_{17}$ ceramic. The discussion of the processing, microstructure, and property relations was based on the results of density measurements, X-ray diffraction (XRD), scanning electron microscopy (SEM), and microwave dielectric measurements.

2. Experimental procedure

Dielectric ceramic powders of $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ and $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ were prepared through the solid-state reaction method. Raw materials, including high-purity (>99.9% purity) $CaCO_3$, Nb_2O_5, TiO_2, SnO_2, and ZrO_2 (all from Alfa; reagent grade), in proportions according to the compositions of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ($x = 0$, 0.1, 0.3, 0.5, 0.7, 0.9, and 1.0) and $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ ($x = 0$, 0.1, 0.3, and 0.5) powders, were mixed and milled in a methyl alcohol solution, using polyethylene jars and zirconia balls, for 24 h. The milled slurries were dried overnight in an 80 °C oven, and then the dried powders were calcined at 1200 °C for 4 h. The calcined powders were re-milled in methyl alcohol for 24 h, and subsequently phase identified using XRD analysis (Rigaku DMX-2200). The calcined $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ and $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ powders were mixed with a 5 wt% of 15% PVA solution and then pressed into disc-shaped compacts under a uniaxial pressure of 120 MPa. The ceramic compacts were heat treated at 550 °C for 4 h to remove the PVA, followed by sintering at temperatures from 1400 °C to 1600 °C for 4 h at a heating rate of 10 °C/min.

The sintered densities of the samples were determined using a liquid displacement method. Phase identification of the ground powders of the sintered ceramics was performed using XRD. Microstructure examination was carried out on the sintered, as well as the fractured, surfaces of the samples using SEM (Hitachi S4700) and energy dispersive spectroscopy (EDS). The permittivities and unloaded Q values at microwave frequencies were measured in the $TE_{01\delta}$ mode using the Hakki and Coleman method [13–15] with a network analyzer (HP 8722ES). The temperature coefficients of the resonance frequency τ_f were measured at temperatures ranging from 25 to 85 °C.

3. Results and discussion

Mixtures of raw oxide materials in proportions according to the compositions of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ and $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ formulas were calcined at 1200 °C. XRD results of the former calcined powders displayed a pure monoclinic $Ca_5Nb_4TiO_{17}$ phase (JCPDS Card No. 51-0412) with no second phase present for $x \leq 0.5$, and with second phases of an orthorhombic $CaSnO_3$ (JCPDS Card No. 31-0312) and a cubic $Ca_{1.3}Sn_{1.6}Nb_{1.2}O_7$ (JCPDS Card No. 37-0191) for $x > 0.5$. XRD results of the latter calcined powders were indexed to be an orthorhombic $Ca_2Nb_2O_7$ phase (JCPDS Card No. 70-2006), and indicated the absence of a second phase. The calcined powders were pelletized, binder burned-out, and then sintered at temperatures between 1400 °C and 1600 °C. Fig. 1(a) presents the relative densities of $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramics sintered at different temperatures. Densification of a pure $Ca_5Nb_4TiO_{17}$ ceramic was observed to be achieved at 1550 °C. With the incorporation of Sn4+ ions at the Ti^{4+} sites, the sintering temperature of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramic was increased slightly to 1575 °C for $x = 0.1$ to

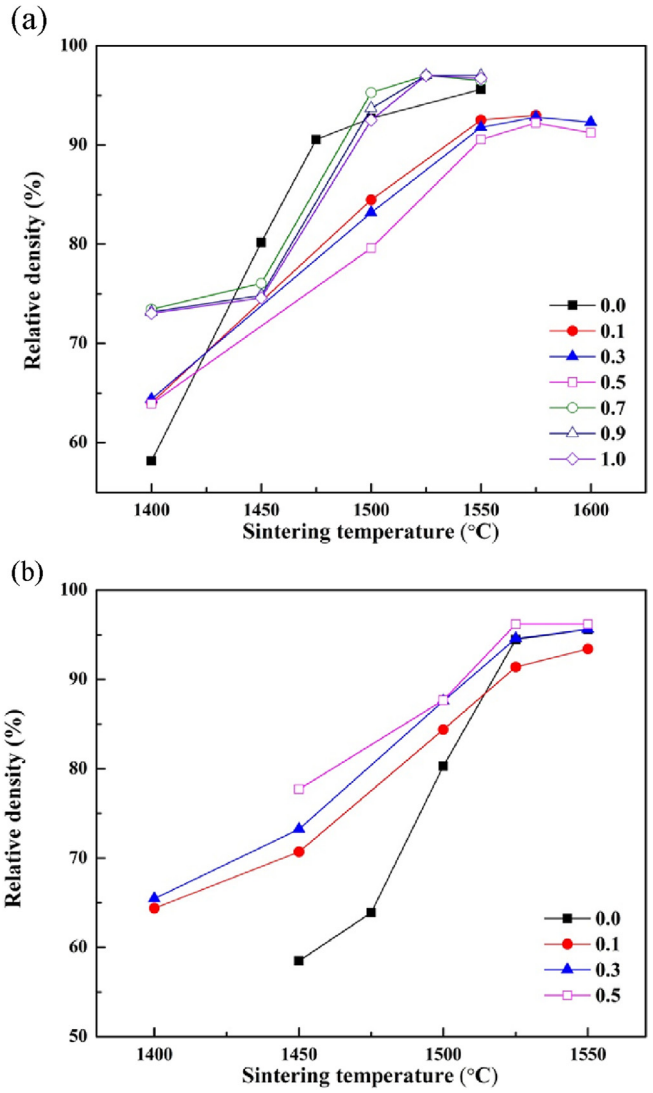

Fig. 1. Relative densities of (a) $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ and (b) $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ ceramics sintered at different temperatures.

0.5. Further increasing the x value above 0.5, the temperature for achieving the maximum density of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramic was reduced to 1525 °C, which was probably owing to the existence of the second phases $CaSnO_3$ and $Ca_{1.3}Sn_{1.6}Nb_{1.2}O_7$ in the calcined powders. For the ceramics sintered at temperatures beyond the maximum densification temperature, the density degraded, because of the presence of trapped voids. The maximum densities of the $Ca_5Nb_4Ti_{1-x}Sn_xO_{17}$ ceramics for $x \geq 0.7$ were much larger than those of other samples, primarily due to the fact that the molecular weight of Sn (118.69 g/mol) is much larger than that of Ti (47.90 g/mol), and partly caused by less residual porosity. Fig. 1(b) plots the relative densities of $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ ceramics that were sintered at various temperatures and had x values up to 0.5. As observed, the partial replacement of Ti^{4+} ions by Zr^{4+} ions did not significantly change the densification behavior of the $Ca_5Nb_4TiO_{17}$ ceramic, although the Zr^{4+} substitution slightly assisted the sintering at low temperatures. All the prepared $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ ceramics were found to achieve their maximum densities at 1550 °C. The maximum sintered density of the $Ca_5Nb_4Ti_{1-x}Zr_xO_{17}$ ceramics increased slightly with increasing Zr^{4+} content, simply due to the slightly higher molecular weight of Zr (91.22 g/mole), compared with Ti.