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Microwave dielectric properties of low loss microwave dielectric ceramics: $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn, Co)

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Abstract

The microwave dielectric properties of low-loss $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn, Co) ceramics prepared by the solid-state route had been investigated. The influence of various sintering conditions on microwave dielectric properties and the structure for $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn, Co) ceramics were discussed systematically. The $Zn_{0.5}Ti_{0.5}NbO_4$ ceramic (hereafter referred to as ZTN) showed the excellent dielectric properties, with $\varepsilon_r = 37.4$, $Q \times f = 194{,}000$ (GHz), and $\tau_f = -58$ ppm/°C and $Co_{0.5}Ti_{0.5}NbO_4$ ceramic (hereafter referred to as CTN) had $\varepsilon_r = 64$, $Q \times f = 65{,}300$ (GHz), and $\tau_f = 223.2$ ppm/°C as sintered individually at 1100 and 1120 °C for 6 h. The dielectric constant was dependent on the ionic polarizability. The $Q \times f$ and τ_f are related to the packing fraction and oxygen bond valence of the compounds. Considering the extremely low dielectric loss, $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co) ceramics could be good candidates for microwave or millimeter wave device application.

Keywords: $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn, Co) ceramics; Microwave dielectric properties; Microstructure

1. Introduction

Recently, a larger number of microwave dielectric ceramics with high dielectric constant (ε_r), low dielectric loss, and stable temperature coefficient of the resonant frequency (τ_f) characteristics had been investigated and reported to satisfy the application in microwave communication systems. Owing to the carrier frequencies of signals extended to higher frequency bands, the microwave dielectric materials with low loss (high $Q \times f$ value) had attracted great attention in the microwave and millimeter wave region.

In this regard, the Li_2O–Nb_2O_5–TiO_2 ceramics system had been studied as a potential candidate material for use in wireless communication systems because of its excellent microwave dielectric properties ($\varepsilon_r = 55$–78, $Q \times f$ values up to 9000 GHz, and a tunable τ_f).[1,2] $Li_{2+x}Ti_{1-4x}Nb_{3x}O_3$ ceramics with $\varepsilon_r = 19.5$, $Q \times f = 84{,}868$ GHz, and $\tau_f = -1.4$ ppm/°C ($x = 0.07$) can be also formed in the Li_2O–Nb_2O_5–TiO_2 system.[3] Liao et al. changed Li_2O–Nb_2O_5–TiO_2 system from Li_2O to NiO to get the excellent microwave dielectric properties for Rutile structure $Ni_{0.5}Ti_{0.5}NbO_4$ (ε_r of 56.8, $Q \times f$ of 21,100 GHz, and τ_f of 79.1 ppm/°C) sintered at 1100 °C for 6 h.[4] In this paper, low-loss microwave dielectric materials $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co), which were made by substituting Ni for Zn and Co in A-site, had been investigated, and their microwave dielectric properties had been discussed. According to the XRD analyses, $Zn_{0.5}Ti_{0.5}NbO_4$ performs ixiolite structure indexed as $ZnTiNb_2O_8$ (JCPDS #48-0323). The $ZnTiNb_2O_8$ ceramics with a fully disordered α-PbO_2 structure were first described by Baumgarte et al. in 1992, and its microwave dielectric properties were reported by Kim et al. as follows: ε_r of 34.3, $Q \times f$ of 42,500 GHz, and τ_f of −52 ppm/°C. However, there have been no reports about the effects of different sintering time and temperatures on their microwave dielectric properties, and the correlation between structure and microwave dielectric properties.[5–7] Many researchers attempted to clarify the relation between structure and microwave dielectric properties of materials because the properties directly depend on structure.[8,9]

The present paper attempted to investigate the novel low-loss $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co) ceramics and discuss the

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effect of different sintering conditions on microwave dielectric properties. Moreover, the influence of $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co) ceramics structure on microwave dielectric properties is also investigated.

2. Experimental procedure

Samples of $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co) were synthesized using conventional solid-state methods from dried high-purity oxide powders (>99.9%): ZnO, CoO, Nb_2O_5, and TiO_2. After grounding under distilled water for 12 h in a ball mill with agate balls, the mixtures were dried, forced through a 200-mesh sieve, and then calcined at 900 °C for 3 h. The calcined powders were remilled with agate balls for 12 h in distilled water and dried. The dried powders with 3 wt.% of a 10% solution of PVA as a binder were screened by a 200-mesh again. The final powders were pressed uniaxially under 150 MPa into disk pellets with a diameter of 11 mm and thickness of 5 mm. The pellets were sintered in air at temperatures ranging from 1060 to 1140 °C for 2–8 h to evaluate the densification behavior. Both the heating and cooling rates during the sintering process were set at 10 °C/min. For pellets of $Ni_{0.5}Ti_{0.5}NbO_4$, the prepared method was the same as that of $A_{0.5}Ti_{0.5}NbO_4$ (A = Zn and Co). In our previous work,[10] the higher $Q \times f$ value (=70,100 GHz) of NTN than that reported by Liao et al.[4] was obtained because of the additional screening process.

Crystalline phases of the sintered samples were identified using X-ray diffraction (XRD, Siemens D5000) using Cu Kα radiation and a graphite monochromator in the 2θ range of 20–60°. According to the theory of X-ray diffraction, the relation between the inter planar spacing (d_{hkl}) and the diffraction angle (θ) can be expressed.[11] Each ionic position of orthorhombic in unit cell is: A-site cation $\pm(0, Y, 1/4; 1/2, Y+1/2, 1/4)$ and $B/O_1/O_2/O_3$-site cation $\pm(X, Y, Z; X, -Y, Z+1/2; X+1/2, Y+1/2, -Z+1/2; X+1/2, -Y+1/2, -Z)$, and that of tetragonal structure is: A-site cation $\pm(0, 0, Z; 1/2, 1/2, Z+1/2)$, B-site cation (0, 0, 0; 1/2, 1/2, 1/2), and Oxygen ion $\pm(X, X, Z; X, X, -Z; X+1/2, -X+1/2, Z+1/2; X+1/2, -X+1/2, -Z+1/2)$. The bond length of A/B–O atom can be calculated by $\sqrt{[(X_{A/B} - X_O) \cdot a]^2 + [(Y_{A/B} - Y_O) \cdot b]^2 + [(Z_{A/B} - Z_O) \cdot c]^2}$, where $X_{A/B}$, $Y_{A/B}$, $Z_{A/B}$, X_O, Y_O, and Z_O represent the X-, Y- and Z-coordinate of A/B and O atom, respectively.[12] Rietveld refinements of the crystal structures were performed using the Full-Prof program.[13] The reliability of the refinement result was judged by the pattern R factor (R_p), the weighted pattern R factor (R_{wp}) and the goodness of fit indicator (χ^2). The microstructures were characterized using a scanning electron microscopy (SEM, Philips XL40FEG, Eindhoven. The Netherlands) to observe and analyze the surface of sintered samples. The bulk densities of the sintered specimens were measured using the liquid Archimedes method, with distilled water as the liquid. The dielectric constants (ε_r) and $Q \times f$ values at microwave frequencies were measured via the Hakki–Coleman dielectric resonator method, as modified and improved by Courtney.[14,15] The dielectric resonator was positioned between two brass plates to form a cavity-like structure. The temperature coefficient of the resonant frequency (τ_f) was calculated with temperature variation of the $TE_{01\delta}$ mode. The test cavity is placed over a thermostat, and the temperature range used is 20–80 °C, which the heating rate was 1 °C/min, and the residence time is 10 min. The τ_f (ppm/°C) is defined as the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 is the resonant frequency at T_1 and f_2 is the resonant frequency at T_2. It had been reported that the temperature coefficient of the resonant frequency (τ_f) depended on the bond valence. The bond valences between i cation (A- and B-site cation) and oxygen ion, v_{i-O} could be obtained in Eq. (2), and V_i was defined as the sum of all the valences from a given cation i:

$$v_{i-O} = \exp\left(\frac{R_{i-O} - d_{i-O}}{b}\right) \quad (2)$$

$$V_i = \sum v_{i-O} \quad (3)$$

where R_{i-O} and d_{i-O} are the bond valence parameter and the length of a bond between cation i and oxygen atom, and b is taken to be a universal constant equal to 0.37 Å.

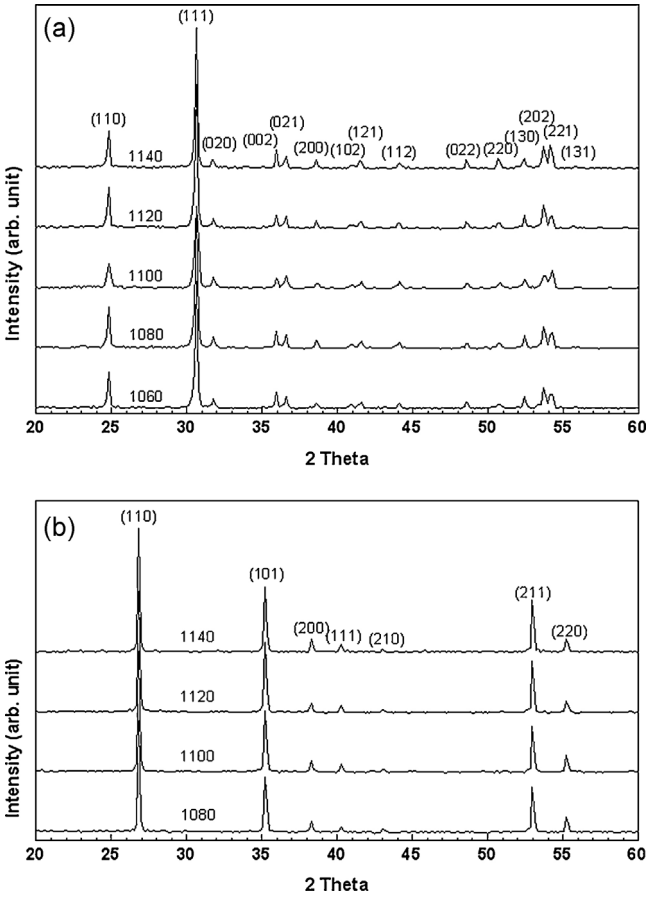

Fig. 1. (a) X-ray diffraction patterns of $Zn_{0.5}Ti_{0.5}NbO_4$ ceramics sintered at 1060–1140 °C for 6 h. (b) X-ray diffraction patterns of $Co_{0.5}Ti_{0.5}NbO_4$ ceramics sintered at 1060–1140 °C for 6 h.