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Journal

Dielectric Properties of $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ Ceramic System at Microwave Frequency

Hanxing Liu, Hongtao Yu,† Zhongqing Tian, Zhenghua Meng, Zhaohui Wu, and Shixi Ouyang

State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

The microwave dielectric properties of the $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ ceramic system have been investigated. The ceramic samples sintered at 1300°–1450°C for 4 h in air exhibit orthorhombic pervoskite and form a complete solid solution for different x value. When the x value increased from 0.2 to 0.8, the permittivity ε_r decreased from 115 to 42, the unloaded quality factor $Q \times f$ increased from 5030 to 13 030 GHz, and the temperature coefficient τ_f decreased from 336 to −28 ppm/°C. When $x = 0.7$, the best combination of dielectric properties, a near zero temperature coefficient of resonant frequency of $\tau_f \sim -6$ ppm/°C, $Q \times f \sim 10\,860$ GHz and $\varepsilon_r \sim 51$ is obtained.

I. Introduction

THE proliferation of commercial wireless technologies, such as cellular phones, global positioning systems, and satellite broadcasting, has placed increasing demands on the performance of dielectric resonators in the microwave frequency range. These microwave dielectric ceramics must combine a high relative permittivity ($\varepsilon_r > 25$) with a low dielectric loss, which means a high-quality factor ($Q \times f > 5000$ GHz) and a near zero temperature coefficient of resonant frequency ($\tau_f \approx 0$ ppm/°C). These three parameters concerning the properties of microwave dielectrics are correlated to the resonator size, frequency selectivity, and temperature stability of the system, respectively. Each dielectric property requires precise control to satisfy the demands of microwave circuit designs. Various compounds such as $Ba_2Ti_9O_{20}$, (Zr, Sn)TiO_4, $Ba(Mg_{1/3}Ta_{2/3})O_3$, and BaO–Ln_2O_3–TiO_2(where Ln is a lanthanum) have been researched and have found application in the microwave communications.[1–4] Another practicable way of obtaining a suitable ceramic is to mix two compounds, one with a positive and the other with a negative temperature coefficient, to form a solid solution or mixture phases to obtain a zero temperature coefficient of resonant frequency. Mixed ceramic approaches can be categorized into three groups:

(1) *Anomalous behavior*: Solid solution between complex perovskites in which the dielectric properties increase or decrease to outside the range exhibited by the end members such as $Ba(Ni_{1/3}Nb_{2/3})O_3$–$Ba(Zn_{1/3}Nb_{2/3})O_3$.[5]

(2) *Linear change*: Solid solution between simple perovskites in which the microwave dielectric properties vary linearly with compositions such as $SrZrO_3$–$SrTiO_3$ and $CaZrO_3$–$CaTiO_3$.[6]

(3) *Nonmonotonic mixture-like behavior*: Solid solution between $A^{2+}B^{4+}O_3$ and $A^{2+}(B_1^{2+}B_2^{5+})O_3$ or $A^{2+}(B_1^{3+}B_2^{5+})O_3$ such as $CaTiO_3$–$Ca(Mg_{1/3}Nb_{2/3})O_3$[7] and $CaTiO_3$–$Pb(Fe_{1/2}Nb_{1/2})O_3$.[8]

This paper investigates two ceramics in the third category. The perovskite $CaTiO_3$ ceramics exhibit dielectric properties of $\varepsilon_r \sim 170$, $Q \times f$ value ~ 3600 GHz, and a large positive $\tau_f \sim 800$ ppm/°C,[6] and the $Ca(Zn_{1/3}Nb_{2/3})O_3$ ceramics possess dielectric properties of $\varepsilon_r \sim 35$, $Q \times f$ value $\sim 16\,000$ GHz, and a negative $\tau_f \sim -43$ ppm/°C.[9] The purpose of the present study is to develop a new dielectric compound, which has high dielectric, high quality factor and near to zero τ_f by incorporating $Ca(Zn_{1/3}Nb_{2/3})O_3$ into $CaTiO_3$, and to study the variation of microwave dielectric properties of the ceramic system $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ as a function of composition (x).

II. Experimental Procedure

$(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ powders with compositions of $x = 0.2$, 0.4, 0.6, 0.7, and 0.8 were prepared using the conventional ceramics processes by a two-stage calcinations procedure. As starting materials, highly pure $CaCO_3$, TiO_2 (99%), ZnO (99.5%), and Nb_2O_5 (99.99%) were used. First, the powders of $CaTiO_3$ and $Ca(Zn_{1/3}Nb_{2/3})O_3$ were individually prepared according to the appropriate molar ratio, and ground in ethanol for 12 h in a ball mill with agate balls in ethanol. The prepared powders were dried and calcined in an alumina crucible at 1200°C for 4 h in air, respectively. Second, the calcined powders were mixed for 10 h according to the molar fraction $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ ($x = 0.2$, 0.4, 0.6, 0.7, 0.8) in a ball mill with 5% PVA as a binder. These powders were pressed into pellets of 12 mm diameter and 6 mm thickness under a uniaxial pressure of 200 MPa. After debinding, these pellets were sintered in alumina crucibles at 1300°–1450°C for 4 h in air. The sintering temperatures were chosen to obtain the highest bulk density for each composition.

The crystalline phases of the prepared samples were investigated by powder X-ray diffraction (XRD, Rigaku D/Max-YB) and the surfaces of the sintered samples were observed by a scanning electron microscope (SEM, Akashi Seisakusho Jsm-5610LV). The bulk densities of the sintered pellets were measured by the Archimedes method. The relative permittivity (ε_r) and the quality factor ($Q \times f$) at microwave frequencies were measured using an HP8722ET network analyzer. The temperature coefficient of resonant frequency was obtained by measuring the resonant frequency of the $TE_{01\delta}$ mode at 20°C (f_{20}) and 80°C (f_{80}).

III. Results and Discussion

The $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ system is observed to exhibit an orthorhombic perovskite structure like the $CaTiO_3$-

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†Author to whom correspondence should be addressed. e-mail: yuhongtao2001@163.com

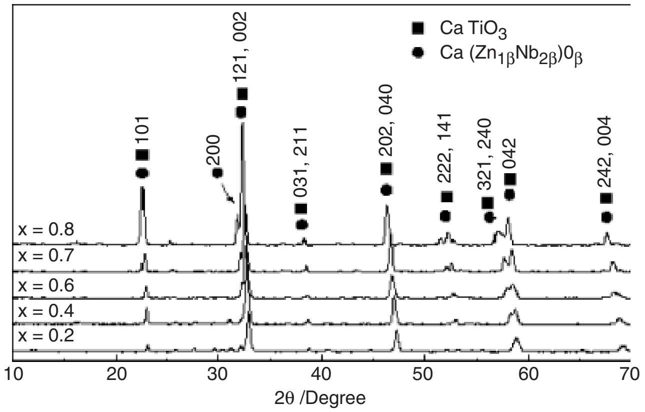

Fig. 1. X-ray diffraction of the $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ system sintered at 1400°C for 4 h.

Table I. Unit-Cell Volume (V_m) and Relative Density of the $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ System

x values	Sintering conditions	V_m (Å^3)	X-ray density (g/cm^3)	Measured density (g/cm^3)	Relative density (%)
0.2	1400°C for 4 h	226.41	4.20	4.05	95.7
0.4	1400°C for 4 h	230.11	4.34	4.20	96.8
0.6	1350°C for 4 h	234.02	4.47	4.34	97.1
0.7	1350°C for 4 h	235.84	4.54	4.41	97.2
0.8	1350°C for 4 h	238.10	4.59	4.49	97.8

Table II. Dielectric Properties of the $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ System

x values	Sintering conditions	L (mm)	D (mm)	f_0 (GHz)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0.2	1400°C for 4 h	10.02	5.50	3.60	115	5030	336
0.4	1400°C for 4 h	10.06	5.60	4.68	76	7560	164
0.6	1350°C for 4 h	10.10	5.60	5.86	62	9540	25
0.7	1350°C for 4 h	10.10	5.10	6.07	51	10860	−6
0.8	1350°C for 4 h	9.98	5.30	6.94	42	13030	−28

type, and a single-phase structure is obtained for all compositions in Fig. 1. Because of the larger lattice parameter of $Ca(Zn_{1/3}Nb_{2/3})O_3$, the unit-cell volume of all compounds increases and the diffraction peaks shift to lower angles as x increases. And it is well known that the porosity is closely related to the permittivity and a low porosity is essential to obtain high quality factor. As the x value increases, the measured density increases and is larger than 95% of the theoretical density obtained from XRD. The relative density of each compound is illustrated in Table I, and all samples in the present study have homogeneous grain growth.

Figure 2 shows the measured results (solid line) and calculated results (dotted line) for the dielectric constants ε_r of the researched ceramic system. The ε_r value of the well-sintered ceramics decreases nonlinearly from 115 to 42 as the x value increases from 0.2 to 0.8. Although the $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ system forms a complete solid solution, as shown by the XRD patterns in Fig. 1, its mixture-like behavior is similar to that observed for $(1-x)CaTiO_3$–$xCa(Mg_{1/3}Nb_{2/3})O_3$[7] and $(1-x)LaAlO_3$–$xSrTiO_3$.[10] The calculated permittivity values were obtained using the empirical rule: $\varepsilon_i^{-1} = v_1\varepsilon_1^{-1} + v_2\varepsilon_2^{-1}$,[10] where v_i and ε_i are the volume fraction and dielectric constant of each end member.

The unloaded quality factor $Q \times f$ and the temperature coefficient of resonant frequency τ_f of the $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ system vary from 5030 to 13 030 GHz and from 336 to −28 ppm/°C, respectively, as x increases in Fig 3. For

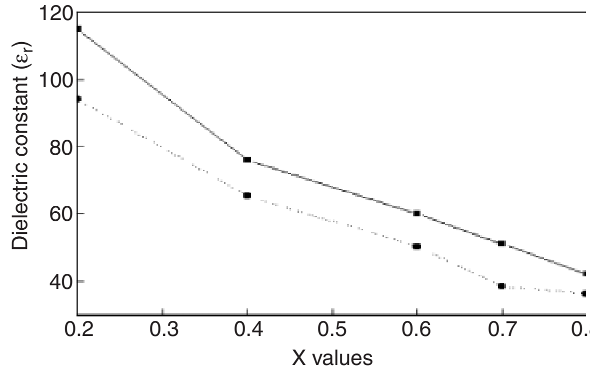

Fig. 2. Dielectric constants (solid line: measured results; dotted line: calculated results) of the $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ system ($x = 0.2$ and 0.4: 1400°C/4h, $x = 0.6$, 0.7, and 0.8: 1350°C/4 h).

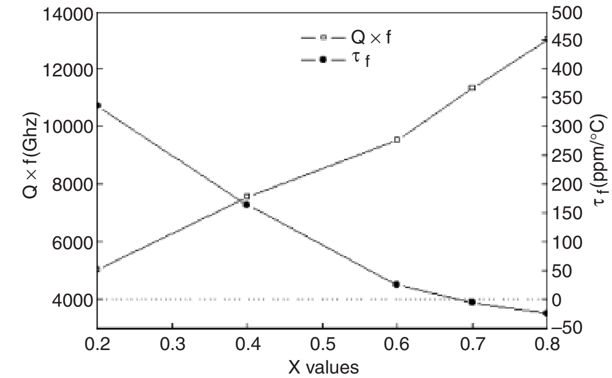

Fig. 3. Qf values and τ_f of the $(1-x)CaTiO_3-xCa(Zn_{1/3}Nb_{2/3})O_3$ system ($x = 0.2$ and 0.4: 1400°C/4 h, $x = 0.6$, 0.7, and 0.8: 1350°C/4 h).

practical application, a composition with suitable microwave dielectric properties is obtained when $x = 0.7$. For this composition the dielectric properties are $\varepsilon_r \sim 51$ and $Q \times f \sim 10\,860$ GHz with a near zero temperature coefficient of resonant frequency of $\tau_f \sim -6$ ppm/°C. The details of dielectric properties of the $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ ceramics are listed in Table II.

IV. Conclusions

The microwave dielectric properties of single-phase ceramics from the $(1-x)CaTiO_3$–$xCa(Zn_{1/3}Nb_{2/3})O_3$ system, prepared by a solid-state reaction method, have been investigated. When the x value increases from 0.2 to 0.8, the dielectric constant ε_r decreases from 115 to 44, while the unloaded quality factor value $Q \times f$ increases from 5030 to 13 030 GHz. The temperature coefficient of resonant frequency τ_f varies in a wide range from 336 to −28 ppm/°C. When $x = 0.7$, the best combination of dielectric properties, a near zero temperature coefficient of resonant frequency of $\tau_f \sim -6$ ppm/°C, $Q \times f \sim 10\,860$ GHz, and $\varepsilon_r \sim 51$, is obtained.

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