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Structure and dielectric properties of Bi_2O_3–ZnO–CaO–Ta_2O_5 ceramics

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Abstract

The effects of chemical substitution of Ca^{2+} cation on the structure and the microwave dielectric properties of BiZnTa-based ceramics were investigated. The relations between B-site partially substituting in $Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$ and dielectric properties especially the temperature coefficient of dielectric constant were evaluated. The phase structure was studied by XRD and microstructure by SEM techniques. The crystal structure of the un-substituted $Bi_2(Zn_{1/3}Ta_{2/3})_2O_7$ was characterized as monoclinic zirconolite-like structure. With increasing amount of Ca^{2+} cation substitution, the crystal structure gradually transforms from monoclinic zirconolite-like structure to a co-existing phase structure with fluorite and BCT phase.

Keywords: C. Dielectric properties; Bismuth zinc tantalum; Cation substitution; Phase structure

1. Introduction

Among bismuth-based ceramics, Bi_2O_3–ZnO–Nb_2O_5 (BZN) ternary oxides have been received special attention and investigated widely in the past year [1–6]. This system features two structurally distinct compounds $Bi_{1.5}ZnNb_{1.5}O_7$ (α-BZN) and $Bi_2Zn_{2/3}Nb_{4/3}O_7$ (β-BZN), which exhibit very dissimilar dielectric properties. Recent studies combined electron, X-ray, and neutron powder diffraction techniques to elucidate the crystal structures of these compounds revealed that their structures are pyrochlore and zirconolite-like structures, respectively [2,7]. Yao and co-workers [4–6] have reported that pyrochlore compound in BZN system shows excellent properties: low sintering temperature, high dielectric constant, and compositionally adjustable temperature coefficients of capacitance. Matjaz and Davies [3] reported the effect of cation substitutions on the structure and dielectric properties of the two bismuth zinc niobate polymorph (α-BZN and β-BZN) and attempted to correlate the changes in chemistry to the temperature coefficients of dielectric constant. Levin et al. [2] reported that the β-BZN compound crystallizes with a monoclinic zirconolite-like structures, which were described as a distorted pyrochlore structure with a pseudo-orthorhombic unit cell. Analogous to the BZN systems, there are two major structural variations in Bi_2O_3–ZnO–Ta_2O_5 (BZT) systems: a cubic pyrochlore based on the $Bi_{1.5}ZnTa_{1.5}O_7$ (α-BZT) composition; a lower symmetry zirconolite phase based on the $Bi_2Zn_{2/3}Ta_{4/3}O_7$ (β-BZT) composition. Recently, BZT systems were studied as candidate materials for microwave dielectrics [8,9].

In the present work, we investigated the dielectric properties of the monoclinic zirconolite structure of the β-BZT system and attempted to modify the temperature coefficients of dielectric constant (α_ε, ppm/°C) by cation substitution of the $Bi_2Zn_{2/3}Ta_{4/3}O_7$ structure. In this paper, we reported our work of partial replacement of Zn^{2+} cation with Ca^{2+} cation and the effect on dielectric properties. The chemical formula of the system is $Bi_2(Ca_{y/3}\ Zn_{2/3-y/3}Ta_{4/3})O_7$ (BCZT) ($0 \leq y \leq 1.0$).

2. Experimental procedures

The starting materials were Bi_2O_3, ZnO, Ta_2O_5 and $CaCO_3$ powders with high purity above 99%. All of the compositions in BCZT system were prepared using solid-state reaction techniques. The oxide powders were weighed in appropriate ratios and mixed in de-ionized water using ZrO_2 milling media in polyethylene containers. The slurries were dried at 120 °C for 15 h and calcined in a closed alumina crucible at 800 °C for 4 h. The calcined powders were

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ball-milled again, dried, granulated through 200-mesh sieve and pressed into pellets of 12 mm in diameter and 2 mm in thickness using PVA as binder. Another kind of specimens was formed into 12 mm diameter and 6 mm thickness, used for microwave properties measurements. The green pellets were then heated and sintered at 950–1100 °C for 4 h in a sealed alumina crucible. The density was determined by the Archimedes' method (buoyancy method).

X-ray diffraction was performed using Bruker D8 X-ray diffractometer with Cu radiation filtered through Ni. A scanning electron microscope was used for microstructure characterization. For the low frequency dielectric characterization, the sintered thin disks were polished. Silver paste was applied and baked as electrodes. The dielectric properties of silver-plated pellets were measured by a high precision LCR meter (Hewlett-Packard 4284A) in conjunction with a computer-interfaced temperature chamber at temperatures range from +160 to −60 °C. Temperature coefficient of dielectric constant was calculated from the slope of dielectric constant in the temperature range of 20–85 °C and the dielectric constant at 20 °C. Dielectric characteristics at microwave frequencies were measured by Hakki and Coleman's dielectric resonator method, as modified and improved by Courtney [10]. A cylindrically shaped dielectric resonator was positioned between two brass plates. A KEITHLEY 6517A high resistance meter was used to measure the electrical resistivity.

3. Results and discussion

Fig. 1 is the X-ray diffraction patterns of the $Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$ with different y value. The basic compound corresponds to $Bi_2Zn_{2/3}Ta_{4/3}O_7$ composition. The $Bi_2Zn_{2/3}Ta_{4/3}O_7$ has a pattern similar to that of $Bi_2Zn_{2/3}Nb_{4/3}O_7$ and could be indexed with monoclinic zirconolite structure [2]. According to XRD pattern, the main crystalline phase remained monoclinic zirconolite structure when Zn^{2+} cation was partially substituted by Ca^{2+} cation less than 0.5/3 M, i.e., $0 < y < 0.5$. With the value of y increasing, a phase with fluorite structure was detected. Furthermore, we investigated the complete substitution of Ca^{2+} for Zn^{2+} at a quantity up to $y = 2$. The composition $Bi_2Ca_{2/3}Ta_{4/3}O_7$ denoted as BCT phase has a different XRD pattern from the $Bi_2Zn_{2/3}Ta_{4/3}O_7$. The phase compositions and crystal structures of the sample could not be elucidated at present. The intermediate compositions ($0.5 < y < 2$) exhibited two-phase even three-phase coexisted. The ionic radius of the Ca^{2+} cation (0.1 nm in VI coordination) is much larger than the Zn^{2+} cation (0.074 nm in VI coordination) [11]. When Ca^{2+} cation substitution into the $Bi_2(Zn_{2/3}Ta_{4/3})O_7$ structure, the range of solid-solution formation for $Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$ was very limited ($y < 0.5$). Multiple phase assemblages formed for high Ca content composition. Compositions of the compounds significantly alter the crystal structure of the materials.

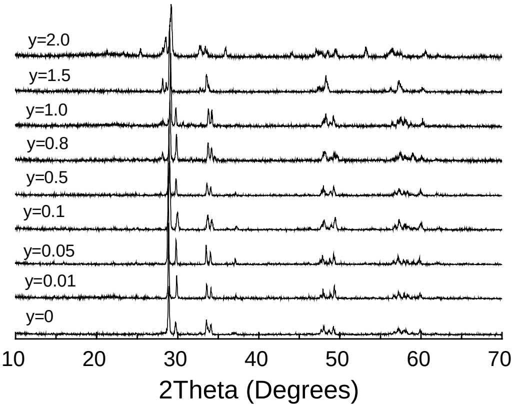

Fig. 1. XRD patterns for $Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$ with $y = 0$–2 compositions sintered at 1030 °C for 4 h.

Microstructure of the β-BZT and the BCT sample is shown in Fig. 2. The SEM revealed marked differences between the two samples. The apparent large planar grains were observed for the BCT samples sintered at 1030 °C. The samples yield larger grains with a strong platy habit compared with the β-BZT samples. The planar grains may be corresponding to the BCT phase. These results were consistent with the results observed using XRD.

The temperature dependence of the dielectric constant (ε) and dissipation factor ($\tan\delta$) both β-BZT and BCT at radio frequency is shown in Fig. 3. For β-BZT sample, with decreasing of temperature, ε continuously decreases at a slow rate. With decreasing of temperature, ε first decreases then increases slightly in BCT sample.

Table 1 summarized the change of dielectric properties versus Ca content y in $Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$. For all compositions, the electrical resistivity was large than 10^{13} Ω cm and the dissipation factor at 1 MHz was smaller than 10×10^{-4} excepting for the BCT sample. The apparent density of the sample sintered at 1030 °C decreases gradually with the Ca content increasing. It can be seen that, the dielectric constants increase from 63 to 70 and the temperature coefficients decrease from 75 to −22 ppm/°C as the Ca content increased. Within the ranges of solid solution, i.e., with low amount of cation substitution ($0 < y < 0.5$), the dielectric properties remained similar to those of the un-substitution sample. In accordance with the XRD, when $0.5 < y < 2$ in BCZT, the change of the dielectric properties might be due to the mixed phase or the secondary phase. As the composition contains a second phase, the Q value was much reduced. The Qf value of the compositions of $0.5 < y < 2$ became smaller than that of composition of $0 \leq y \leq 0.5$.

As we saw in the Table 1, it was suitable for compensating the α_ε value, when a proper concentration of Ca^{2+} was introduced to substitute Zn^{2+} in the BCZT compound. With $y = 0.8$, BCZT gave a dielectric constant of ∼67.5, a Q value of ∼2127 and a α_ε value of ∼14 ppm/°C at 1 MHz.

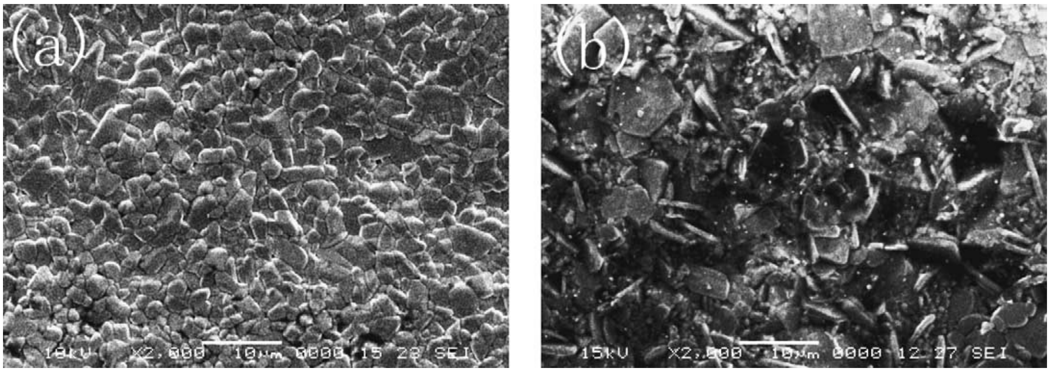

Fig. 2. The surface morphology of (a) the β-BZT sample and (b) the BCT sample sintered at 1030 °C for 4 h.

Table 1
Dielectric properties of the BCZT ceramics at room temperature

$Bi_2(Ca_{y/3}Zn_{2/3-y/3}Ta_{4/3})O_7$	ε (20 °C, 1 MHz)	$\tan\delta$ ($\times 10^{-4}$, 1 MHz)	ε (20 °C, GHz)	$\tan\delta$ ($\times 10^{-4}$, GHz)	α_ε (ppm/°C)	Density (g/cm^3)	ρ (Ω cm)	Qf (GHz)
$y = 0$	63.0	1.0	61.5 (5.59)	8.0	75	8.717	$\geq 10^{13}$	6987
$y = 0.01$	63.4	2.7	61.0 (5.27)	8.4	97	8.701	$\geq 10^{13}$	6275
$y = 0.05$	63.5	4.1	60.8 (4.98)	10.5	99	8.691	$\geq 10^{13}$	4743
$y = 0.1$	63.7	4.3	62.0 (5.06)	10.8	96	8.675	$\geq 10^{13}$	4663
$y = 0.5$	66.3	4.8	62.7 (5.04)	25	25	8.615	$\geq 10^{13}$	2007
$y = 0.8$	67.5	4.7	63.5 (5.16)	42	14	8.570	$\geq 10^{13}$	1229
$y = 1.0$	67.5	5.1	64.3 (4.96)	51	8.0	8.462	$\geq 10^{13}$	970
$y = 1.5$	68.6	7.2	66.5 (4.95)	77	−7.5	8.319	$\geq 10^{13}$	644
$y = 2.0$	70.0	16.7	67.5 (4.53)	85	−22	8.212	$\geq 10^{13}$	533

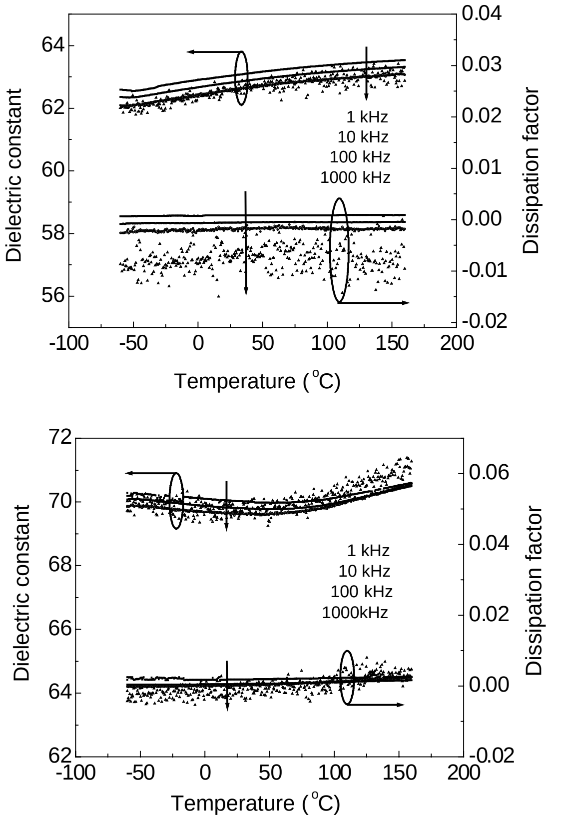

Fig. 3. Temperature dependence of dielectric constant and dissipation factor for β-BZT and BCT.

Comparing with bismuth-based cubic pyrochlore such as α-BZN, less attention was paid to the β-BZN in the previous study. One of the reasons probably is that the cubic pyrochlore structure is able to accommodate a wide range of cation and anion substitutions; but the solid solubility of β-BZN is very limited for all substitutions [3]. We observed a similar effect in the β-BZT. But the β-BZT or β-BZN exhibits a higher Q value as compared with α-BZT or α-BZN at microwave frequencies. Among the potential microwave dielectrics within the limits of bismuth-based ceramics, β-BZT display better properties than α-BZT at microwave frequencies.

4. Conclusions

The dielectric properties of BCZT ceramics were studied at microwave frequencies. The observed microwave dielectric properties were, $\varepsilon =\sim 61.5$, $Q =\sim 1250$ at ∼5.6 GHz with $\alpha_\varepsilon =\sim 75$ ppm/°C at 1 MHz for β-BZT, and $\varepsilon =\sim 67.5$, $Q =\sim 118$ at ∼4.5 GHz with $\alpha_\varepsilon =\sim -22$ ppm/°C at 1 MHz for BCT. With lower amount of Ca^{2+} cation substitution ($0 < y < 0.5$), the crystal structure was still monoclinic zirconolite structure. With increasing of Ca content substitution ($0.5 < y < 2$), the crystal structure gradually transforms from monoclinic zirconolite structure to a co-existing phase structure with fluorite phase. If Ca^{2+} cation substituted for Zn^{2+} cation entirely, the BCT phase was detected. The phase structure of BCT is very different from the β-BZT.

The dielectric properties change regularly with the structure accordingly.

Acknowledgements

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