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Structure and microwave dielectric properties of $Ba_{1+x}[(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}]O_3$ $(-0.015 \leq x \leq 0.015)$

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Abstract

The sintering behavior, ordering state and microwave dielectric properties of $Ba_{1+x}(Zn_{0.3}Co_{0.7})_{1/3}Nb_{2/3}$ Ceramics ($-0.015 \leq x \leq 0.015$) were investigated in this paper. The X-ray diffraction (XRD) results show that all samples exhibit a single phase except for the sample with $x = -0.015$. Scanning electron microscopy (SEM) observation and energy dispersion analysis (EDS) indicate that the second phase is barium niobate. Raman spectrum reveal the presence of long range order (LRO) of B-site ions when $-0.015 \leq x < 0$ and only short range order (SRO) when $0 \leq x \leq 0.015$. The sinterability is decreased for the samples with $x > 0$. The dielectric constant slightly decreases when $x < 0$ and decreases greatly when $x > 0$. The $Q \times f$ value of the samples with $x > 0$ is much lower than that with $x < 0$. The maximum $Q \times f$ value of 70,917 GHz is obtained when $x = -0.01$. The temperature coefficient of resonant frequency exhibits positive value for the samples with $x \geq 0$ and negative value for the samples with $x < 0$. Near zero temperature coefficient of resonant frequency was obtained when $x = 0.002$.

Keyword: Nonstoichiometric

1. Introduction

With the development of wireless communication, especially the third generation telecommunication (3G), low cost microwave dielectrics with high Q factor are desired. Requirements for these dielectric materials must be the combined microwave dielectric properties of high dielectric constant ($\varepsilon_r > 30$), high unload quality factor ($Q \times f > 40{,}000$ GHz) and a temperature coefficient of the resonant frequency (τ_f) tunable through zero. Recently dielectric resonators of Nb-based compounds with a complex perovskite structure have been extensively studied due to their very high quality factor in microwave frequency and relative low cost compared with Ta-based complex perovskite ceramics.[1–4] Among these materials, $Ba(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}O_3$ (BCZN) has been reported to possess high dielectric constant ($\varepsilon_r \sim 34.5$), a high Q value ($Q \times f = 56{,}000$–$97{,}000$ GHz) and small temperature coefficient of resonant frequency ($\tau_f \sim 0$).[3] However, its Q value is very sensitive to processing conditions. The poor reproducibility of Q values was considered to be related to the difficult control of the B-site ordering degree and valence state of Co.[2] The effect of B-site doping on the structure, sinterability and microwave dielectric properties of BCZN have been investigated by Azough et al.[5–6] It is well established that the Q values of complex perovskite ceramics increase with the increase of B-site cation ordering degree. It was reported that the B-site ordering degree of $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) and $Ba(Zn_{1/3}Nb_{2/3}O_3$ (BZN) was enhanced by the introduction of small amount of A-site deficiency.[7,8]

In this research paper, the effect of A-site nonstoichiometry on the densification, microstructure, structural ordering, and microwave dielectric properties of $Ba(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}O_3$ is investigated.

2. Experiment

$Ba_{1+x}[(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}]O_3$ $(-0.015 \leq x \leq 0.015)$ ceramic samples were prepared by conventional solid-state reaction process from the starting materials including Nb_2O_5 (99.9%), CoO (99.8%), $BaCO_3$ (99.7%, impurities of Ca^{2+} and Sr^{2+} are less than 0.15 wt.%) and ZnO (99.6%). The $Ba_{1+x}[(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}]O_3$ $(-0.015 \leq x \leq 0.015)$ compounds were weighed and mixed with ZrO_2 balls in ethanol for 24 h, dried and calcined at the temperature of 1150 °C for 2 h in a alumina crucible. The calcined powders were grounded, dried and mixed with 7 wt.% PVA. The mixtures were pressed into

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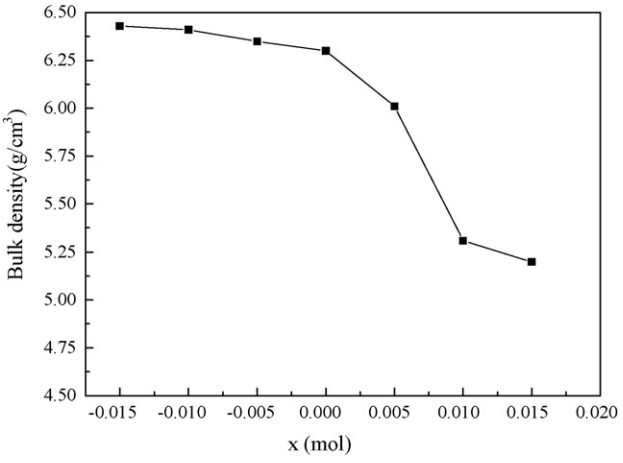

Fig. 1. Variation of bulk density of samples sintered at 1450 °C/10 h as function of x value.

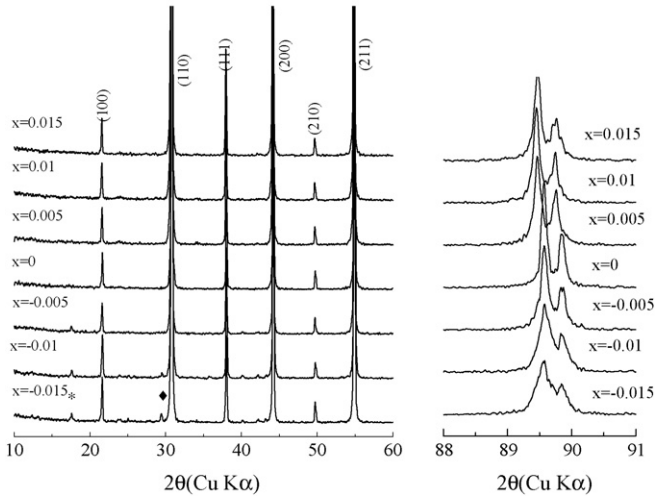

Fig. 2. XRD patterns of the sintered specimens with different x value: (*, superlattice reflection caused by B-site ordering; ♦, reflection caused by second phase).

pellets. The compacts were sintered between 1450 °C for 10 h. In order to prevent the Co and Zn evaporation loss, the compacts were muffled with powder of the same composition. A cooling rate of 100 °C/h was employed.

The phase constitutes of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered Cu Kα radiation (40 kV and 20 mA, Model Dmax-RC, Japan). In order to avoid the influence of the second phases formed on the surface during sintering, the surface of the specimen for XRD was abraded. Powder diffraction patters were taken for $60° < 2\theta < 140°$ with 0.01° step scanning for precise lattice parameter measurement. Silicon powders were mixed as an internal standard. Bulk density of the sintered specimens was identified by Archimedes' method. The Raman experiments were carried out for the sintered samples (Model Jobin Y'von U1000). A laser line of 532 nm and 500 mW average power was used. The spectra were recorded from 0 to 1000 cm^{-1}. The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM) (Model XL20, Philips Instruments, Netherlands). All samples were polished and thermal etched at the temperature which was 200 °C lower than its sintering temperature. Microwave dielectric properties of the sintered samples were measured between 7 and 8 GHz using network analyzer (Hewlett Packard, Model HP8720C, USA). The

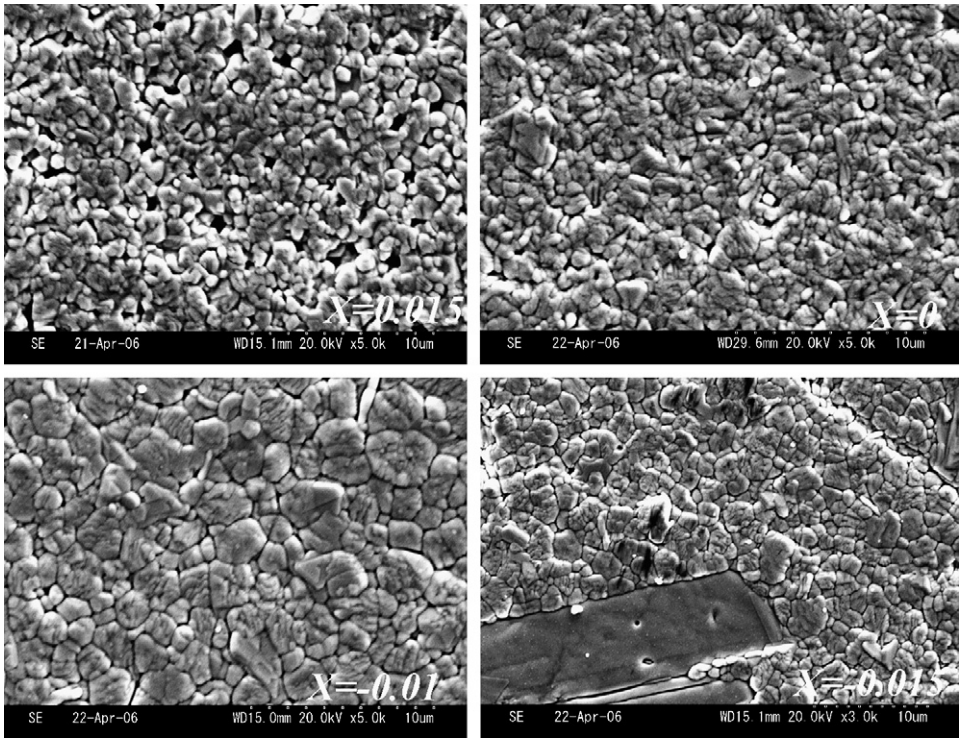

Fig. 3. SEM photographs of specimens with different x value sintered at 1450 °C/10 h.