

Improvement of microwave dielectric properties for Ba(Ni_{1/3}Nb_{2/3})O₃ ceramics by Zr-substitution

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Abstract

Effects of Zr-substitution on the structure, microstructure and microwave dielectric properties of Ba(Ni_{1/3}Nb_{2/3})O₃ ceramics have been investigated. A small amount of Zr-substitution facilitates the densification of Ba(Ni_{1/3}Nb_{2/3})O₃ ceramics. Within $x \leq 0.05$, the densification temperature decreases with increasing x in Ba[(Ni_{1/3}Nb_{2/3})_{1-x}Zr_x]O₃, while it turns to increase for $x > 0.05$. With increasing x , the grains become more homogeneous and closely contacted, and significantly increase in size for $x=0.15-0.20$. The B-site cations 1:2 ordering is destroyed by Zr-substitution, and only stabilizes for $x \leq 0.04$. B-site cations 1:1 ordering starts to form in $x=0.04$, and the 1:1 ordering degree first increases and then decreases with increasing x . Qf value decreases slightly in $x=0.01$ and then increases monotonously with x increasing from 0.02 to 0.20. The destroyed 1:2 ordering structure is responsible for the decreased Qf value in $x=0.01$, while the improved grain configuration dominates the increase of Qf value for $x=0.02-0.20$. The dielectric constant ϵ_r increases monotonously with increasing x , due to the higher polarizability of Zr ion than the average value of Ni/Nb ions. The temperature coefficient of resonant frequency τ_f shifts from negative to positive through zero with increasing x , which is ascribed to the highly positive τ_f value of the end member BaZrO₃. The significant improvement of microwave dielectric properties has been achieved for $x=0.10$, higher ϵ_r , higher Qf as well as near zero τ_f value have been obtained: $\epsilon_r=31.8$, $Qf=36,100$ GHz, $\tau_f=7.8$ ppm/°C.

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1. Introduction

In the modern world, wireless communication covers a wide field including mobile phone, GPS, DBS TV and so on. Higher data processing speed and further bulk miniaturization are the two main trends in the development of these applications. To support such developing trends, demands on new material systems or designs for the wireless communication system are ever increasing. Microwave dielectric ceramics, which are used for manufacturing resonators and filters in the wireless communication system, have attracted interests of material scientists for a few decades due to their importance in the wireless communication system. To function as a resonator, microwave dielectric ceramics should possess such properties as high

dielectric constant (ϵ_r), high unloaded quality factor (Qf), and near-zero temperature coefficient of resonant frequency (τ_f). These properties correspond to miniaturization (the size of a resonator is reciprocal to $\sqrt{\epsilon_r}$), high frequency selectivity, and temperature stability of the system.

The Ba(B'_{1/3}B''_{2/3})O₃-based complex perovskite ceramics (B' = Mg, Zn, Co, and Ni; B'' = Ta, and Nb) are good candidates for the wireless communication applications due to their excellent properties in microwave range [1–4]. Disordered and 1:2 ordered arrangements of B-site cations are the most common structures in Ba(B'_{1/3}B''_{2/3})O₃. In the former, B' and B'' cations distribute randomly in the O₆ octahedra, while in the latter, they repeat in a 1:2 {...B'B''B''...} sequence along one of the <111> directions in the parent cubic cell. However, 1:1 ordered structure can also form, depending on the processing conditions and cation substitutions [5–8]. The chemical ordering of B-site cations has been proved to dominate the microwave properties, especially the

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Q_f value [6,9–12]. It is well known that a high degree of B-site cations 1:2 ordering is critical for obtaining high Q_f value. However, an important exception comes from the effects of Zr-substitution. Tamura et al. reported that a small amount of Zr-substitution (4%) reduces the 1:2 ordering degree while increases the Q_f value of $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ [13]. The exception was not well explained until Davies and Tong reproduced the same system and performed further investigation by transmission electron microscopy (TEM), they suggested that improvement of Q_f value was derived from the stabilization of the domain boundaries and the lowering of the free energy of the antiphase boundaries [7]. Zr-substitution has also been applied to other related complex perovskite systems, such as $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [8], $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [14], and $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ [15]. Different results for the Q_f value have been found among these systems. For example, 5 mol% substitution of Zr produces a 100% improvement in the Q_f value of $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, while the Q_f value of $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ degrades severely with Zr-substitution. The degradation of Q_f value for $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ is explained in terms of lower ordering degree due to the lower order–disorder temperature, which contradicts the explanation for $\text{Ba}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$ – BaZrO_3 system. In addition, it is noticed that the order–disorder temperature of $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (~ 1375 °C) [16–18] is lower than that of $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (1400 °C in Ref. [15]), but the Q_f value of the former does not decrease as the latter with Zr-substitution. Such phenomenon implies that there are still some contradictions in the effects of Zr-substitution on the Q_f value of $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ ceramics as well as the mechanisms for explaining them. Therefore, it is an important issue to clarify the factors that dominate the microwave dielectric properties in the Zr substituted $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ systems, especially the Q_f value. Moreover, though Zr-substitution resulted in obvious improvement of Q_f value for $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ and $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$, the problem of large τ_f values in them was not solved, for example, the τ_f of $\text{Ba}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ increased to 60 ppm/°C for 35% Zr-substitution.

Another member of the $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ family, $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$, which possesses a largely negative τ_f value, was also investigated as a candidate for the microwave dielectric resonators [19,20]. It has been used as a compensation for those analogs which have largely positive τ_f values [21–23]. However, few efforts have been made to improve the microwave dielectric properties separately for $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$, especially, to our best knowledge, no investigation on the Zr-substitution for $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ has been reported. Based on the reported results for Zr substituted $\text{Ba}(\text{B}'_{1/3}\text{B}''_{2/3})\text{O}_3$ systems, it can be concluded that Zr-substitution mainly improves the Q_f value, increases ϵ_r and shifts the τ_f value towards positive. Therefore, it can be expected that Zr-substitution will tune the largely negative τ_f value (-18 ppm/°C in Ref. [19]) to near zero for $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ accompanied by the increasing of the Q_f value and ϵ_r . Meanwhile, the $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – BaZrO_3 system is also an ideal model for clarifying the different results between $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – BaZrO_3 and other analog systems, since the order–disorder temperature of $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (1450–1500 °C) [19] is similar to that of $\text{Ba}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$.

In this study, Zr-substitution is applied in an attempt to improve the microwave dielectric properties of $\text{Ba}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$

O_3 ceramics. The effects of Zr-substitution on the structure, microstructure and microwave dielectric properties are systematically investigated. Especially, the particular evolution of structure with Zr-substitution is revealed by Raman spectroscopy and transmission electron microscopy (TEM). The variations of microwave dielectric properties are discussed by linking to the cation ordering, grain configuration and the polarizability, in order to clarify the factors which dominate the microwave dielectric properties.

2. Experimental procedure

$\text{Ba}[(\text{Ni}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Zr}_x]\text{O}_3$ ceramics ($x=0$ – 0.20) were prepared via a standard solid-state reaction method, using highly-pure carbonate and oxide powders: BaCO_3 (99.99%), NiO (99.0%), Nb_2O_5 (99.99%), and ZrO_2 (99.99%). Stoichiometric quantities of the raw powders were weighted and mixed by ball milling with zirconia balls and ethanol as grinding media in plastic jars for 24 h. The mixtures were calcined at 1200 °C in air for 3 h after drying. The calcined powders were milled again for 24 h, then granulated with ~ 6 wt% polyvinyl alcohol (PVA) and pressed into cylindrical pellets of 12 mm in diameter and 2–6 mm in thickness under a pressure of about 98 MPa. The green pellets were sintered at 1400–1575 °C (depending on the compositions) in air for 3 h to yield ceramics. After cooling down to 1100 °C at a rate of 2 °C/min, the as-sintered ceramics were cooled down to room temperature naturally inside the furnace. For comparison, compositions of $x=0.50$, 0.70, 0.90 and 1.0 were also prepared through the same route. The calcination temperature was 1200 °C, and the sintering temperature was 1650–1690 °C. The densification temperature, where the nearly full densification (relative density $> 98\%$ T.D., T.D. represents the theoretical density) was obtained, was discussed as the function of composition.

The phase purity and structure parameters of the as-sintered ceramics after crushing and grinding were determined by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (RIGAKU D/max 2550/PC, Rigaku Co., Tokyo, Japan). The microstructures of the present ceramics were observed by the scanning electron microscopy (SEM) (SIRION-100, FEI Co., Eindhoven, Netherlands). Samples for transmission electron microscopy (TEM) were prepared by mechanically grinding the ceramic pellets to a thickness of around 30 μm , and then breaking into small pieces. In order to reduce surface charging, a small piece of sample was selected to attach to a copper ring with dimensions of 3 mm in outer and 0.8 mm in inner diameters. Then a final thinning was conducted via argon-ion milling. The selected area electron diffraction (SAED) patterns and dark-field images were obtained using a transmission electron microscopy (JEM2100F, JEOL, Tokyo, Japan) at 200 kV. The pellets were polished to a roughness of around 0.5 μm and subjected to Raman measurements at room temperature using a Raman spectrometer (Lab.HR800, Jobin Yvon, Paris, France) with Ar laser line of 514.5 nm as the excitation source. The spectra were recorded from 50 to 1000 cm^{-1} .

The dielectric constant ϵ_r and quality factor Q were evaluated by the Hakki–Coleman method [24] and cavity method [25] using

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