# New microwave dielectric ceramics with near-zero $\tau_f$ in the $Ba(Mg_{1/3}Nb_{2/3})O_3$-$Ba(Ni_{1/3}Nb_{2/3})O_3$ system

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For the application of dielectric ceramics to a microwave device, a high dielectric constant ($\varepsilon_r$), a near-zero temperature coefficient of resonant frequency ($\tau_f$) and a high $Q$-value are required. Ceramics of the general formula $Ba(B'_{1/3}\ B''_{2/3})O_3$ ($B' = Mg$, Zn, Ni or Co; $B'' =$ Ta and Nb) have attracted a great deal of attention because of their interesting microwave properties [1–6]. Ta-based complex pervoskite materials such as $Ba(Mg_{1/3}\ Ta_{2/3})O_3$ and $Ba(Zn_{1/3}\ Ta_{2/3})O_3$ were candidate materials and used commercially [1, 2]. Unfortunately, the cost of $Ta_2O_5$ is very high. Therefore, a large number of Nb-based complex pervoskite materials have been reported in the scientific literature because $Nb_2O_5$ is comparatively cheap [3–6]. In these compounds, $Ba(Mg_{1/3}Nb_{2/3})O_3$ (BMN) exhibits good microwave properties: $\varepsilon_r = 32$, $Q = 5600$ (10.5 GHz) and $\tau_f = 33$ ppm/°C [6]. However, the large $\tau_f$ value makes it virtually useless for most applications. The value of $Ba(Ni_{1/3}Nb_{2/3})O_3$ (BNN), which has the same complex pervoskite structure, was found to be −18 ppm/°C [5]. This gives rise to an attractive proposition: whether the near-zero $\tau_f$ value can be attained in BMN-BNN system.

In this letter, the microstructure and microwave dielectric properties of $(1 - x)$BMN $- x$BNN system were investigated. The main object of this investigation is to gain a new microwave dielectric ceramics with near-zero $\tau_f$ in the BMN-BNN system.

Ceramics of composition $(1 - x)$BMN $- x$BNN were prepared by a two-stage calcinations procedure. Firstly, BNN and BMN powders were synthesized at 1100 °C for 2 hrs and 1300 °C for 4 hrs respectively. Secondly, BMN and BNN powders were mixed and ball-milled in a polyethylene jar with agate balls in ethanol for 24 hrs. Then the dried powders were pressed into pellets with dimensions of 12 mm diameter and about 6 mm thick under a pressure of 200 Mpa. Finally, the pellets were sintered at 1450 °C in air for 4 hrs the microstructures of the sintered samples were investigated by using X-ray diffraction (XRD) (Model D/MAX-RB, RIGAKU Corporation, Japan), scanning electron microscopy (SEM) (Model JSM-5610LV, Jeol Ltd., Japan). The densities of the sintered specimens were measured by water-immersion technique. Microwave dielectric properties were measured and the microwave frequency range was measured at 8 GHz using an HP8722ET network analyzer. $Q$ was determined directly from reflection measurements and $\varepsilon_r$ calculated from the resonant frequency and sample dimensions. The resonant frequency was measured in a computer controlled temperature chamber between 25 and 85 °C and the $\tau_f$ was calculated.

Fig. 1 shows the XRD patterns of $(1 - x)$BMN $-$ $x$BNN ceramics. The main diffraction peaks can be indexed on the $Ba(Mg_{1/3}Nb_{2/3})O_3$-type 1:2 ordered hexagonal perovskite with three formula units per unit cell. However, it is also evident that all samples contain small second phase. Second phase peaks are present at about 28.7° and 42.8°2$\theta$, corresponding to a d spacing of 3.11 and 2.11 Å, respectively. Hughes *et al.* observed second phase peaks with similar d spacings to those in Fig. 1 in their study of the microwave dielectric properties in $Ba(Zn_{1/3}Nb_{2/3})O_3$-$Ba(Ga_{1/2}Ta_{1/2})O_3$ system [3].They concluded that ZnO loss from the sample resulted in the formation of a surface niobate phase. During our sintering experiments, a green substance was found on the surface of the crucible. It was evident that the green substance came from NiO volatilization. So it is proposed that an analog of this phase forms during sintering on the surface of $(1 - x)$BMN $- x$BNN pellets.

A typical microstructure of $(1 - x)$BMN $- x$BNN is shown in Fig. 2, it exhibits a very dense microstructure with an average grain size of approximately 1.5 $\mu$m. Second phase is absent in SEM image of the fractured surface. It also demonstrates that NiO loss should be responsible for barium niobate phase.

Fig. 3 shows the experimental density and X-ray density as a function of the composition. The experimental value varies from 6.170 to 6.433 g/cm$^3$, which gives porosity in the range 1.85–4.00%. This is in accordance with the SEM image shown in Fig. 2.

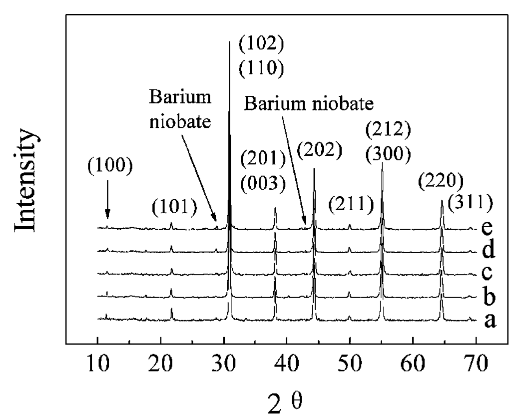


*Figure 1* XRD patterns of $(1 - x)$BMN $- x$BNN solid solutions (a: $x = 0.2$, b: $x = 0.4$, c: $x = 0.5$, d: $x = 0.6$, e: $x = 0.8$).

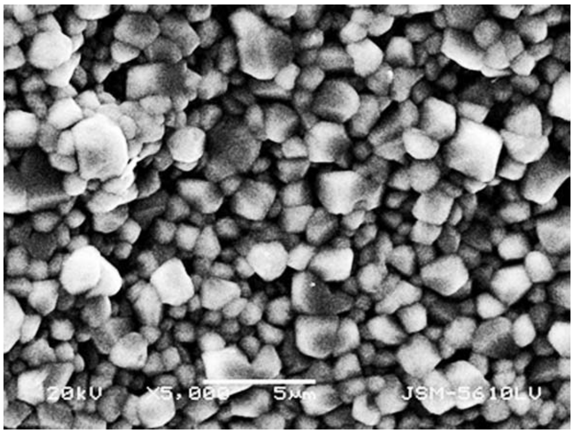


*Figure 2* SEM micrograph of fractured surface micrograph of 0.5BMN-0.5BNN.

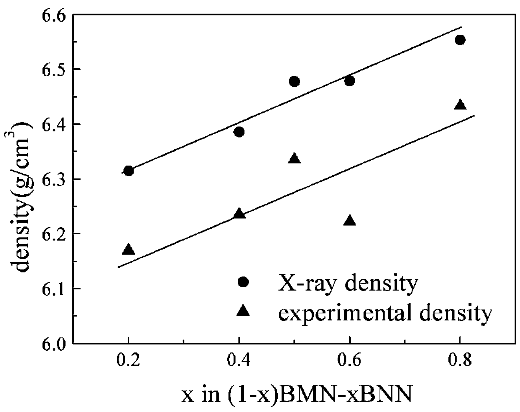


*Figure 3* Density vs composition in system $(1-x)$BMN $- x$BNN.

Fig. 4 shows the microwave dielectric properties of $(1-x)$BMN $- x$BNN ceramics sintered at 1450 °C for 4 hrs. As shown in Fig. 4a, the variation of dielectric constant with $x$ is not significant. For all the specimens, it is about 30.5. On the other hand, the Qf value decreases from 41220 to 36230 as $x$ varies from 0.2 to 0.8. Fig. 4c demonstrates the $\tau_f$ values of the $(1-x)$BMN $- x$BNN ceramic system. The $\tau_f$ value of samples showed an almost linear decrease with $x$. It varied from 17 to $-18.5$ ppm/°C as the $x$ value increased from 0.2 to 0.8 for the $(1-x)$ BMN $- x$BNN ceramics. At $x = 0.5$, a $\tau_f$ value of $-0.55$ ppm/°C was obtained. It is believed that 0.5BMN-0.5BNN system is a potential microwave dielectric ceramics because of its near-zero $\tau_f$. However, the Qf value is only 39 400, lower than pure BMN and BNN. Some optimization of processing is required to modify microstructure and improve Qf value.

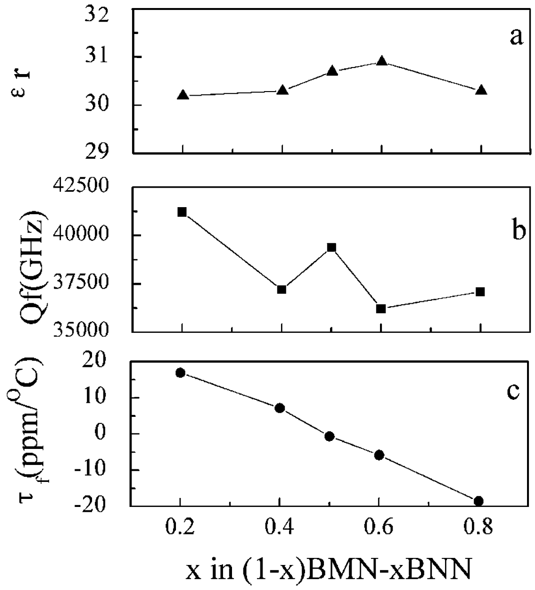


*Figure 4* Microwave dielectric properties as a function of composition of $(1-x)$BMN $- x$BNN ceramics, measured at about 8 GHz (a: dielectric constants, b: Qf value, c: temperature coefficients frequency).

In this study, the microstructure and microwave dielectric properties of $(1-x)$BMN $- x$BNN system were investigated. A new microwave dielectric ceramics with Near-Zero $\tau_f$ in the BMN-BNN system was fabricated. 0.5BMN-0.5BNN solid solution exhibits good microwave properties: $\varepsilon_r = 30.9$, Qf $= 39400$ and $\tau_f = -0.55$ ppm/°C. Further work should be undertaken to improve the Qf value.


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