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SCIENCE DIRECT
Journal of the European Ceramic Society 26 (2006) 1977–1979
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Property control of microwave dielectric materials using self-flux compositions

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Available online 17 November 2005

Abstract

In order to improve the sinterability and controllability of dielectric properties, we focused on self-flux composition. In the case of $Ba(Mg_{1/3}Nb_{2/3})O_3$, we selected $Ba_{(1-\beta)}Nb_{\beta}O_{\delta}$ as self-flux system and investigated correlations between Q-factor and the β value. Interestingly, high Q-value was obtained only at the $\beta = 0.45$. Moreover, the dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f) change linearly with the quantity of $Ba_{0.55}Nb_{0.45}O_{\delta}$ by keeping up high Q-value. As a result, it was indicated that the dielectric properties could be controlled by the assumption of stoichiometric composition and the liquid phase consisted of "self-flux". In a similar way of thinking, it seems that this concept of property designing will be applied to the complex-perovskite-type materials.

Keywords: Dielectric properties; Perovskites; Self-flux

1. Introduction

Because of the rapid progress of high-speed communication technology, microwave dielectric materials with high ε_r, high Q-value and good stability of the τ_f are required for the application in the microwave devices. To meet these requirements complex-perovskite-type dielectric materials, for example, $Ba(Mg_{1/3}Nb_{2/3})O_3$ and $Ba(Zn_{1/3}Ta_{2/3})O_3$, have been investigated.

Generally, it is well known that a deviation from stoichiometric composition of complex-perovskite-type dielectric materials shows significant effects on the Q-value and sinterability.[1–3] Therefore, the properties were improved by substitution of elements and/or by small amount of additives to avoid the problem. The purpose of this study is to improve the sinterability and controllability of dielectric properties. We have been focusing on self-flux compositions, which consist of the constituent element of the dielectric material. In the case of $Ba(Mg_{1/3}Nb_{2/3})O_3$, we selected $Ba_{(1-\beta)}Nb_{\beta}O_{\delta}$ as self-flux system and investigated on correlations between Q-value and the β value.

2. Experimental

High purity powders (>99.9%) were used as starting materials. The powders were weighed and ball-milled using zirconia balls for 15 h with ethanol. After drying, the mixed powders were calcined in air. The calcined powder was used as precursor and mixed with binder by ball-milling. After granulation, the powder was pressed into 15-mm diameter pellets and fired at various temperatures. The crystal states of sintered samples were investigated using Raman spectroscopic analysis (Jobin-Yvon/HORIBA Group, Model Lablam 1B). Polished surfaces of sintered specimens were observed by scanning electron microscopy (JEOL, Model JSM-6460LA). Microwave dielectric properties of the sample were measured by Hakki and Coleman's dielectric resonator method[4] using a network analyzer (Hewlett-Packard, Model HP 8510A).

3. Results and discussion

Fig. 1 shows dependences of $Q(TE_{011})f$ value and sinterable temperature on the composition of $Ba(Mg_{1-x}Nb_x)O_3$. It is shown that Q-value drastically lowers when the Nb quantity increases from stoichiometric composition. Similar to other researchers, it was confirmed that a deviation from stoichiometric composition of complex-perovskite-type dielectric materials shows significant effects on the Q-value. From a different point

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doi:10.1016/j.jeurceramsoc.2005.09.045

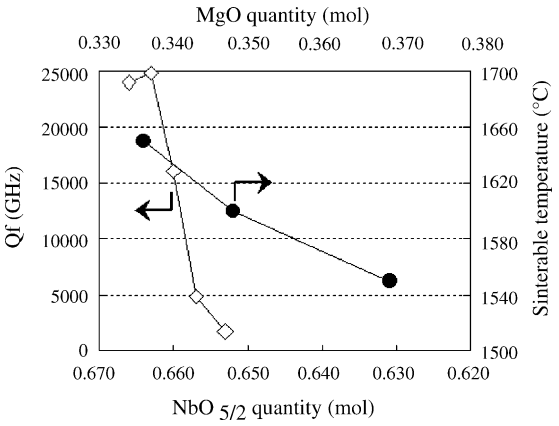

Fig. 1. Dependences of $Q(TE_{011})f$ value and sinterable temperature on the composition of $Ba(Mg_{1-x}Nb_x)O_3$.

$$(1\text{-}\alpha)\underbrace{AE(B^{II}_{1/3}B^{V}_{2/3})O_3}_{\text{Stoichiometric Grain}} - \alpha\underbrace{AE_{1-\beta}B^{V}{}_{\beta}O_{\delta}}_{\text{Self-Flux}}$$

Scheme 1. The chemical composition formula for new concept.

of view, we focused on the improvement of sinterability. From the results of XRD measurement for these samples, major peaks are identified with $Ba(Mg_{1/3}Nb_{2/3})O_3$, and Ba–Nb–O phase newly appears, when the Nb quantity increases. According to phase diagram,[5] it is confirmed that Ba–Nb–O phase forms liquid phase at the sintering temperature. Judging from the above, it is considered that the samples were constituted by stoichiometric grains. Then, we deduced the new concept (Scheme 1 and Fig. 2). In short, the composition of grains maintains the stoichiometry and liquid phase has been formed by the composition of the remainder. Especially, it is possible to call this liquid phase "self-flux", because it has been formed from the prescribe elements. If the "self-flux" functions as a dielectric, the controllability of the dielectric characteristic seems to become possible by the composition and quantity of the liquid phase. At first, this concept was applied to the development of BaO–MgO–$NbO_{5/2}$ system dielectric materials. The result is shown in Fig. 3. The experiment was advanced by the change of liquid phase composition (β) and liquid phase quantity (α). As a result, high Q-value was obtained only at the $\beta = 0.45$ ($Ba_5Nb_4O_{15}$) composition. It was confirmed that this $Ba_{0.55}Nb_{0.45}O_{\delta}$ ($Ba_5Nb_4O_{15}$) ceramic was functioned as a dielectric and showed a $Q(TE_{011})f$ of 13,600 GHz, a ε_r of 39, and a τ_f of 70 ppm/K. It is surprising that high Q-value is obtained even to 30 mol% at the "self-flux" quantity.

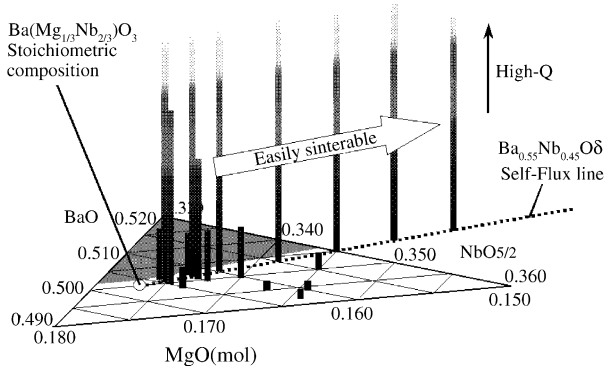

Fig. 3. Distribution of high Q-value region in schematic phase diagram of BaO–MgO–$NbO_{5/2}$ system.

In order to show the liquid phase concretely, $(1-\alpha)Ba(Mg_{1/3}Nb_{2/3})O_3$–$\alpha Ba_{0.55}Nb_{0.45}O_{\delta}$ ($Ba_5Nb_4O_{15}$) samples were fired at long time and observed by SEM as shown in Fig. 4. When the quantity of liquid phase (α) increases, the light-gray region is expanded. It was proven that this part was Ba–Nb–O phase by EDS analysis. Also, Raman spectroscopy can be used to examine the concept. Fig. 5 shows full width half maximum (FWHM) of Raman peak as a function of liquid phase composition (β) and liquid phase quantity (α). It is known that superlattice peak is easy to appear for stoichiometric $Ba(Mg_{1/3}Nb_{2/3})O_3$ and Raman peak at 380 cm^{-1} is consistent with the changes in X-ray superlattice reflections.[6] It is suggested that the fluctuation of the composition does not affect this peak. The results clearly show that the grains maintain the stoichiometric composition.

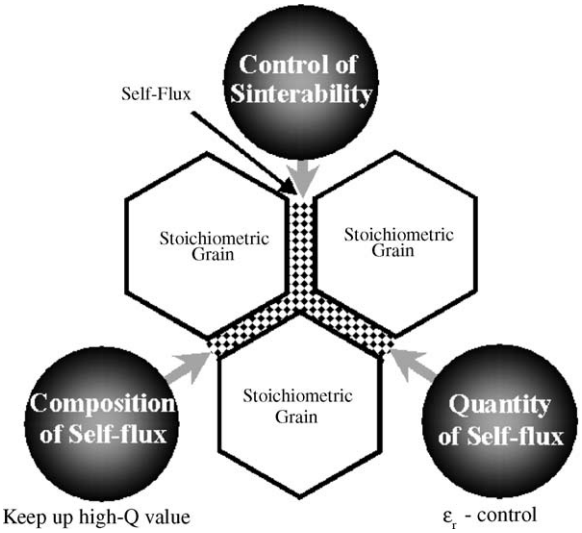

Fig. 2. The conceptual scheme to control dielectric properties.

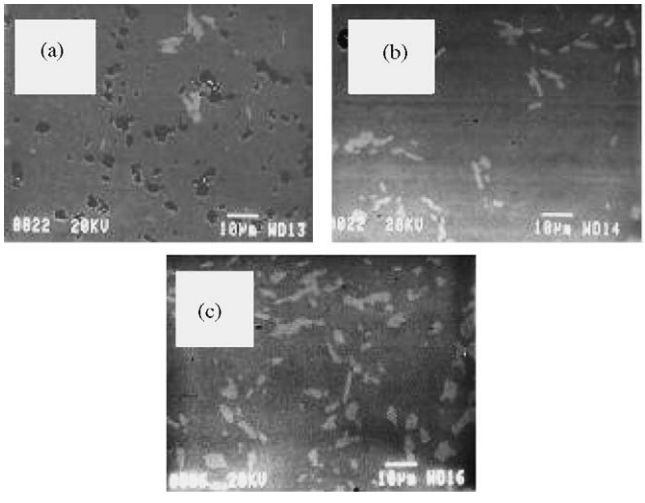

Fig. 4. SEM images for $(1-\alpha)Ba(Mg_{1/3}Nb_{2/3})O_3$–$\alpha Ba_{0.55}Nb_{0.45}O_{\delta}$ samples: (a) $\alpha = 0.097$, (b) $\alpha = 0.209$ and (c) $\alpha = 0.329$.

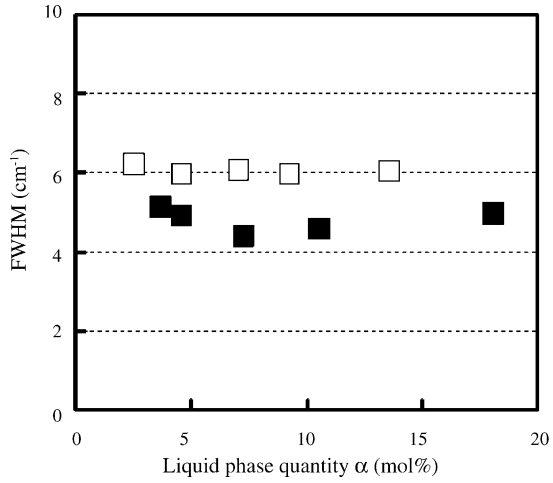

Fig. 5. Raman peak (FWHM) of liquid phase composition (β) and liquid phase quantity (α); (□): $\beta = 0.50$, (■): $\beta = 0.45$.

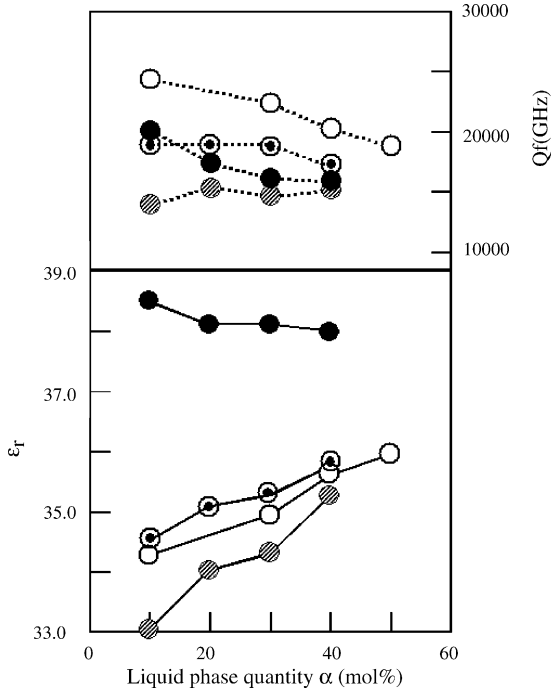

Fig. 6. Microwave dielectric properties of $(1-\alpha)Ba(B^{II}_{1/3}Nb_{2/3})O_3$–$\alpha Ba_{0.55}Nb_{0.45}O_\delta$. B^{II}: (●) Zn, (⦿) Co, (◯) Mg, (◍) Ni.

Therefore, the samples were constituted by $Ba(Mg_{1/3}Nb_{2/3})O_3$ and Ba–Nb–O phase. These results lead us to the conclusion that the concept was supported.

We applied this concept into other composition system and verified the case in which other B^{II} site elements of the perovskite in Scheme 1. Fig. 6 shows microwave dielectric properties of $(1-\alpha)Ba(B^{II}_{1/3}Nb_{2/3})O_3$–$\alpha Ba_{0.55}Nb_{0.45}O_\delta$. The ε_r changes linearly with the quantity of $Ba_{0.55}Nb_{0.45}O_\delta$ by keeping up high Q-value for each B^{II}. Furthermore, ε_r and τ_f are controlled by the "self-flux" quantity. Fig. 7 shows these properties for $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Co_{1/3}Nb_{2/3})O_3$–$Ba_{0.55}Nb_{0.45}O_\delta$ ($Ba_5Nb_4O_{15}$) system as a function of liquid phase quantity. From

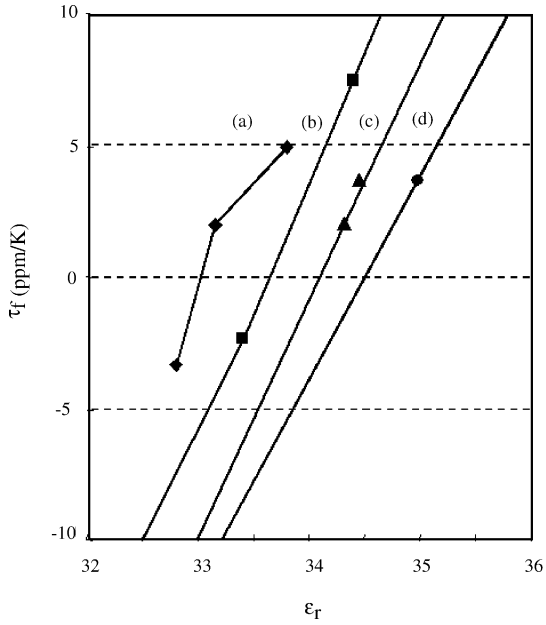

Fig. 7. Dielectric properties of $(1-\alpha)\{Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Co_{1/3}Nb_{2/3})O_3\}$–$\alpha Ba_{0.55}Nb_{0.45}O_\delta$ system controlled by liquid phase quantity (α): (a) $\alpha = 0$, (b) $\alpha = 0.1$, (c) $\alpha = 0.2$ and (d) $\alpha = 0.3$.

these results obtained by using this concept, minor adjustments to optimum dielectric characteristics for each cavity become possible.

4. Conclusions

It was indicated that the dielectric properties could be controlled by the assumption of stoichiometric composition and liquid phase consisted of "self-flux". Furthermore, minor adjustments to optimum dielectric characteristics for each cavity become possible. In a similar way of thinking, it seems that this concept of property designing will be applied to the complex-perovskite-type materials.

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