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Technical report

Improvement of Temperature Coefficient of Frequency in Ba-deficient $Ba_5Nb_4O_{15}$ Microwave Dielectrics

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Ba-deficient non-stoichiometric compositions of $Ba_{5-x}Nb_4O_{15-x}$ ($x=0$ to 0.5) have been investigated for the purpose of improving microwave dielectric properties. While there was no significant variation in dielectric constant, variations in $Q\times f$ and TCF (temperature coefficient of frequency) values with the degree of Ba deficiency were prominent. Near zero TCF value was obtained for the composition of $Ba_{4.77}Nb_4O_{14.77}$. The apparent formation of a second $BaNb_2O_6$ phase for the Ba-deficient compositions was believed as responsible for the improved TCF. It was interesting to note that the second phase was present more preferably inside of the sample.

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1. Introduction

There have been extensive studies in developing new low temperature co-fired ceramic (LTCC) materials, particularly having relatively high dielectric constants >20 for various electronic passive components and module packages.[1)-4)] Due to the restriction of firing temperature below 900°C, an appropriate content of glass was regarded as an essential choice in producing successful LTCC compositions.[5)-7)] At the same time, there have been continuing efforts in developing glass-free LTCC compositions in order to overcome shortcomings, such as high dielectric loss and low dielectric constant, which primarily come from the common silicate glasses.

The BaO–Nb_2O_5 system has been known as one of the promising candidates in providing sufficient densification around 900°C without using glass as a sintering aid.[8),9)] $Ba_5Nb_4O_{15}$ was reported as possessing high $k\sim$40–44, $Q\times f\sim$ 53,000 GHz and TCF$\sim+$50–78 ppm/°C at 16 GHz when fired at 1425°C.[9),10)] Addition of small contents of low melting oxides such as B_2O_3, CuO, V_2O_5 and Bi_2O_3 reduces the sintering temperature from 1425°C to ~900°C. $Ba_5Nb_4O_{15}$ is known to be sensitive to the choice of additive oxides in sustaining the desirable microwave dielectric properties.[11),12)]

The present work intends to demonstrate the beneficial effects of Ba-deficient $Ba_{5-x}Nb_4O_{15-x}$ compositions for the purpose of enhancing TCF while other microwave dielectric properties are kept within the practical ranges, $k>40$ and $Q\times f>15{,}000$ at GHz frequencies. Phase development and its dependence on dielectric properties were discussed with supporting experimental evidences.

2. Experimental procedure

The samples with nominal compositions of $Ba_{5-x}Nb_4O_{15-x}$ with different x values from 0 to 0.5 were prepared by the typical solid state reaction utilizing high-purity $BaCO_3$ (99.9% purity, Aldrich, Milwaukee, WI) and Nb_2O_5 (99.9% purity, Aldrich, Milwaukee, WI). The raw materials were admixed by ball milling in ethanol for 15 h, dried at 120°C in an oven and calcined at 1100°C for 2 h in ambient atmosphere. The calcined powder was mixed with fixed additives of 0.1 mass% Cu_2O and 0.5 mass% B_2O_3 by ball milling. The mixture was dried on a hot plate while stirring with a magnetic bar and then pressed uniaxially at ~80 MPa. An 1.5 mass% polyvinyl alcohol (PVA) solution was used as a binder to make pellets. Sintering was performed by firing pressed pellets at 900°C for 2 h with a fixed heating rate of 5°C/min.

The crystalline phases were determined using an X-ray diffractometer (XRD; Rigaku B/Max-2500/PC, Tokyo, Japan) with CuKα radiation. Microstructures of the sintered samples were examined by scanning electron microscopy (SEM; Model S-4200, Hitachi, Nissei Sangyo, Japan). Bulk density was measured by using the Archimedes principle. The microwave dielectric properties of the sintered samples were measured using a network analyzer (Agilent 8720ES, Palo Alto, CA). The dielectric characteristics such as dielectric constant, k and quality factor, Q were determined by the Hakki-Coleman dielectric resonator method in the S_{21} transmission mode.[13)]

3. Results and discussion

Figure 1 shows the XRD patterns obtained for the $Ba_{5-x}Nb_4O_{15-x}$ samples ($x=0$ to 0.5), sintered at 900°C for 2 h. The pellet samples were grinded into fine powder for the XRD measurement. As expected, only $Ba_5Nb_4O_{15}$ phase was observed for the stoichiometric $Ba_5Nb_4O_{15}$ ($x=0$) whereas all Ba-deficient samples showed the presence of a second phase, i.e., $BaNb_2O_6$. The increase in relative peak intensity of the second phase with increasing x suggests that the percentage of $BaNb_2O_6$ in the sample becomes more apparent with further Ba-deficiency. The peaks of the hexagonal $Ba_5Nb_4O_{15}$ phase tended to shift to higher angles for the Ba-deficient samples. The values of lattice constant calculated were $a=5.815$, $b=5.815$, and $c=11.79\ 10^{-10}$ m for the stoichiometric sample while they changed into $a=5.788$, $b=5.788$, and $c=11.81\ 10^{-10}$ m for the $x=0.1$ sample. The lattice constants were found to vary meaninglessly for the nonstoichiometric samples regardless of x value.

Figure 2(a) shows the intensity changes of $BaNb_2O_6$ phase relative to $Ba_5Nb_4O_{15}$ as a function of Ba-deficiency as expressed by the equation of $I_{BaNb_2O_6(220)}/[I_{Ba_5Nb_4O_{15}(103)}+I_{BaNb_2O_6(220)}]$. $I_{BaNb_2O_6(220)}$ is the intensity of the strongest $BaNb_2O_6$(220) peak and $I_{Ba_5Nb_4O_{15}(103)}$ is the intensity of the strongest $Ba_5Nb_4O_{15}$(103) peak. The intensity ratio gives an idea on the approximate molar content of $BaNb_2O_6$ phase existing at each composition. For example, a ratio value of 0.124 for composition corresponding to $x=0.5$ indicates that

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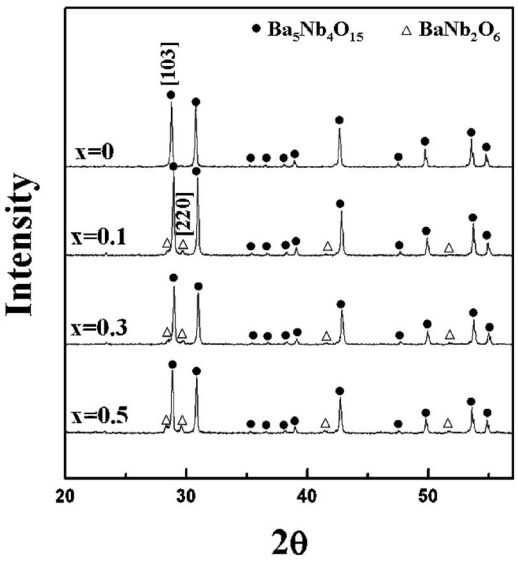

Fig. 1. XRD patterns of $Ba_{5-x}Nb_4O_{15-x}$ samples fired at 900°C for 2 h.

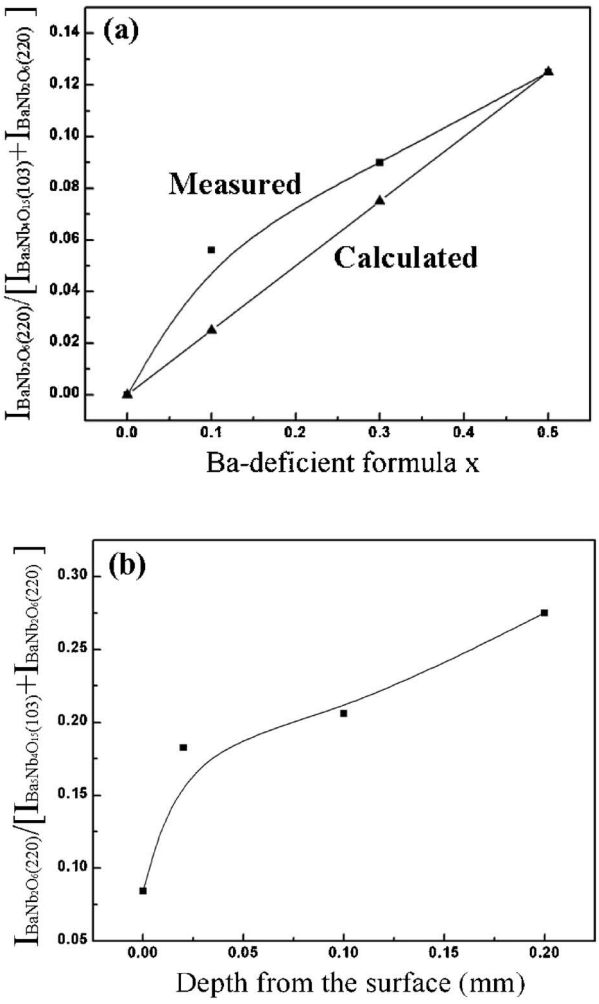

Fig. 2. Relative peak intensity of the $Ba_5Nb_4O_{15}$(103) and $BaNb_2O_6$ (220) samples as a function of (a) Ba-deficiency in $Ba_{5-x}Nb_4O_{15-x}$ (b) depth from the surface of $x=0.5$ sample.

the sample consists of 12.4% $BaNb_2O_6$ and 87.6% $Ba_5Nb_4O_{15}$. Figure 2(a) also represents the calculated intensity ratios from the $Ba_{5-x}Nb_4O_{15-x}$ formula with an assumption that only the two phases are present in all compositions. For example, the calculated ratio of 0.125 for the $x=0.5$ composition was obtained by assuming the molar content (12.5%) of $BaNb_2O_6$, which can exist in the $Ba_{4.5}Nb_4O_{14.5}$ formula. Although some deviations from the measured values were observed in the $x=0.1$ and $x=0.3$ samples, overall increasing tendency seemed to match well with each other. Therefore, the intensity comparison in the XRD patterns may be useful in proposing the relative content of the second phase of $BaNb_2O_6$. It is very difficult to know why the specific samples of $x=0.1$ and $x=0.3$ samples showed deviations from the calculated values. Generally, however, the direct intensity comparison between two phases can not be understood as the exact quantitative basis basically due to the difference in mass absorption between two phases, e.g., $Ba_5Nb_4O_{15}$ and $BaNb_2O_6$ here. In addition, the sensitivity to instrument and sample preparation was thought to contribute potentially to the difference.

Figure 2(b) shows the relative peak intensity of $I_{BaNb_2O_6(220)}/[I_{Ba_5Nb_4O_{15}(103)}+I_{BaNb_2O_6(220)}]$ as a function of distance from the surface for the $x=0.5$ sample. In this case, the sample was polished sequentially up to 0.2mm from the as-fired surface. The XRD patterns were obtained from each polished surface of the sample. It was interesting to note the unexpected variation of phase distribution obtained according to depth from the surface of the pellet. The intensity ratio was found to increase as the depth from the surface increased. Such observation indicates that the second phase, $BaNb_2O_6$, exists more preferably inside of the sample.

Figure 3 illustrates the SEM images of the samples corresponding to $x=0$, 0.1, 0.3 and 0.5 respectively. In each case, the sample was polished by ~0.2 mm from the surface and cleaned ultrasonically in acetone before taking the images. It is found that there is no apparent trend in microstructural characteristics of the samples with different x values. Average grain sizes of the $x=0$ and $x=0.5$ samples, as calculated by the intercept method, were about 0.15 μm and 0.17 μm, respectively. The range of grain size obtained in this study is smaller than the value reported in the literature (1–3 μm) for the $(1-x)Ba_5Nb_4O_{15-x}BaNb_2O_6$ composition with B_2O_3 as an additive, where elongated grains of $Ba_5Nb_4O_{15}$ were dominant with distinctly-distributed $BaNb_2O_6$ grains.[14] However, the present work did not show any distinguishable difference in morphology between the two phases, namely $Ba_5Nb_4O_{15}$ and $BaNb_2O_6$. It is noticeable that unexpected abnormally-grown grains were observed as exemplified in Fig. 3(b) as a triangle symbol. It is believed that the abnormal grains are due to the non-homogeneous distribution of Cu_2O and B_2O_3 used here to reduce sintering temperature.

Figure 4 shows the average values of microwave dielectric properties of $Ba_{5-x}Nb_4O_{15-x}$ samples, sintered at 900°C for 2 h, as a function of Ba-deficiency. It is noticed that the dielectric constant of the samples remains similar over the range of x values while the product of quality factor and resonant frequency ($Q\times f$) and TCF found decreased significantly with the increase in Ba-deficiency. Such changes observed in this study were reasonable when compared with the reported dielectric properties for the two phases, i.e. $Q\times f$ ~53,000 GHz, k~40–44 and TCF~+50–78 ppm/°C for $Ba_5Nb_4O_{15}$ and $Q\times f$~4,000 GHz, k~42 and TCF~–800 ppm/°C for $BaNb_2O_6$.[9)–11)] The similar k values of the two phases are understood as responsible for the insignificant

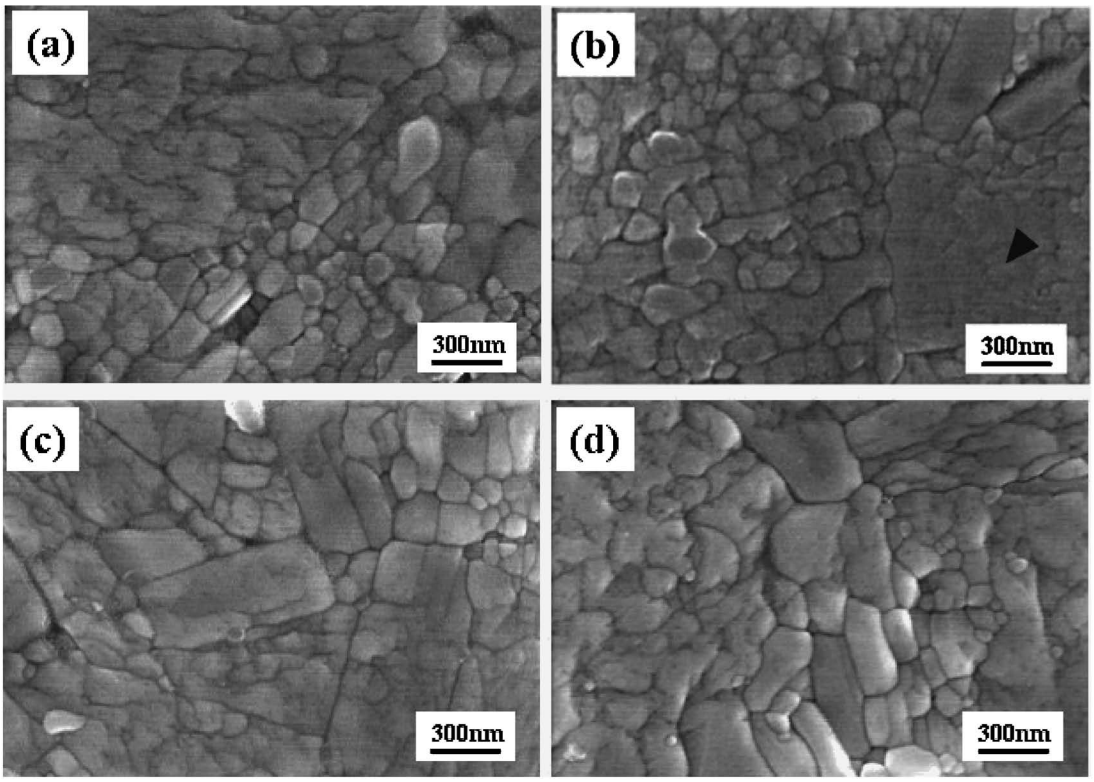

Fig. 3. Microstructures of $Ba_{5-x}Nb_4O_{15-x}$ samples with (a) $x=0$, (b) $x=0.1$, (c) $x=0.3$ and (d) $x=0.5$ samples.

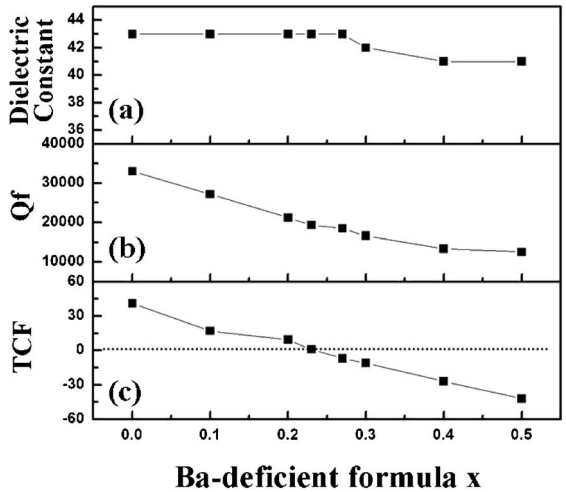

Fig. 4. Variation of dielectric Properties of $Ba_{5-x}Nb_4O_{15-x}$ samples ($x=0$ to 05). (a) dielectric constant, (b) quality factor x resonant frequency and (c) temperature coefficient of frequency.

variation in k value of the $Ba_{5-x}Nb_4O_{15-x}$ samples.[14] The lower $Q\times f$ value of the secondary phase might cause a gradual reduction in the overall $Q\times f$ value of the samples with increase in x. It was interesting to note that the TCF value was near zero when $x=0.23$, corresponding to the 5.8% mole fraction of $BaNb_2O_6$. Near zero TCF was reported for $(1-x)Ba_5Nb_4O_{15-x}BaNb_2O_6$ composition when 16 mol% of $BaNb_2O_6$ was present.[14] $Ba_5Nb_4O_{15}$ phase has a positive TCF where as $BaNb_2O_6$ phase possesses a negative TCF. The negative TCF of the second phase in the non-stoichiometric $Ba_{5-x}Nb_4O_{15-x}$ must be responsible for compensating the positive TCF of $Ba_5Nb_4O_{15}$ phase and eventually for creating the zero TCF. The composition ($x=0.23$) corresponding to zero TCF also exhibited desirable $Q\times f\sim$20,000 GHz and $k\sim$43, which must be suitable for the LTCC applications.

4. Conclusions

Ba-deficient nonstoichiometric $Ba_{5-x}Nb_4O_{15-x}$ ($x=0$ to 0.5) dielectrics have been studied with regard to phase development and microwave dielectric properties. The increase of the second phase, $BaNb_2O_6$, with increasing Ba-deficiency was found to affect final microwave dielectric properties, particularly TCF value. The $Ba_{4.77}Nb_4O_{14.77}$ composition can be highlighted as an optimal one since it demonstrates excellent dielectric properties, such as $k\sim$43, $Q\times f$ $\sim$20,000 GHz and TCF $\sim$0 ppm/°C, as a result of firing at 900°C for 2 h.

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