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Preparation of $BaO\text{-}PbO\text{-}Nd_2O_3\text{-}TiO_2$ Powders by Hydrothermal Synthesis

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Abstract–Homogeneous and nano-sized BPNT [$(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$] powders were prepared under various hydrothermal conditions. Crystallinity and homogeneity of the synthetic powders were investigated. The microwave dielectric properties of the filters prepared with hydrothermal powders were compared with those of the filters prepared with conventional powders. The microwave dielectric properties of the filter prepared with the hydrothermal powders were also better than those of the filter manufactured with the conventional powders. The dielectric constant, quality constant and temperature coefficient of resonance frequency of hydrothermally prepared filter under optimum condition and measured at 3.5 GHz around were about 93, 6067 and 0 ppm/°C, respectively.

Key words: Powder, Hydrothermal, BPNT [$(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$], Microwave, Dielectric

INTRODUCTION

Microwave dielectric materials used in high frequency ranges must have a high dielectric constant (ε_r) with a good quality constant (Q factor) and a low temperature coefficient of resonance frequency (τ_f) [Wu and Chen, 1999]. In order to improve these properties, many researchers have investigated $BaO\text{-}TiO_2$, $BaO\text{-}Re_2O_3\text{-}TiO_2$ (Re: Nd, Sm, La), $(Mg, Ca)TiO_3$, $(Zr, Sn)TiO_4$, $(Ca, Sr, Ba)ZrO_3$ and the complex perovskite compounds of $A(B_{1/3}B'_{2/3})O_3$ (A=Ba, Sr, B=Mg, Zn, Mn, Ni, Ca, Co, B'=Nb, Ta) structure [Ploude et al., 1975; Kolar et al., 1980; Wu and Chen, 1999]. Among these dielectric materials, $BaNd_2Ti_5O_{14}$ showed high dielectric constants with satisfactory Q values, but its temperature coefficients were still large. Wakino, et al. investigated a $BaO\text{-}PbO\text{-}Nd_2O_3\text{-}TiO_2$ (BPNT) system that was modified from $BaNd_2Ti_5O_{14}$ by substituting Pb for Ba in order to improve its dielectric constant and Q value. Notably, the temperature dependency was close to zero in this substitution composition [Wakino et al., 1984].

Typically, BPNT powders are prepared by the solid-state reaction method (referred to as conventional method in this paper). However, this powder preparation brings about defects, such as non-uniformity of particle size, inclusion of contamination and inhomogeneous composition of powders during processing. The main advantage of hydrothermal method in powder preparation is directly to synthesize homogeneous, highly fine and narrowly dispersed particles more easily with good uniformity in composition [Seo and Kong, 2000; Cho and Lee, 2001].

In this study, microwave dielectric materials of $BaO\text{-}PbO\text{-}Nd_2O_3\text{-}TiO_2$ (BPNT) powders (referred to as BPNT in this paper) were prepared under hydrothermal conditions, and the characteristics of the products were compared with those produced by the conventional method.

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‡This paper is dedicated to Professor Wha Young Lee on the occasion of his retirement from Seoul National University.

EXPERIMENTAL

1. Powder Preparation

Fig. 1 shows the flow diagram of the experiments for the preparation of BPNT powders by both the conventional and hydro-

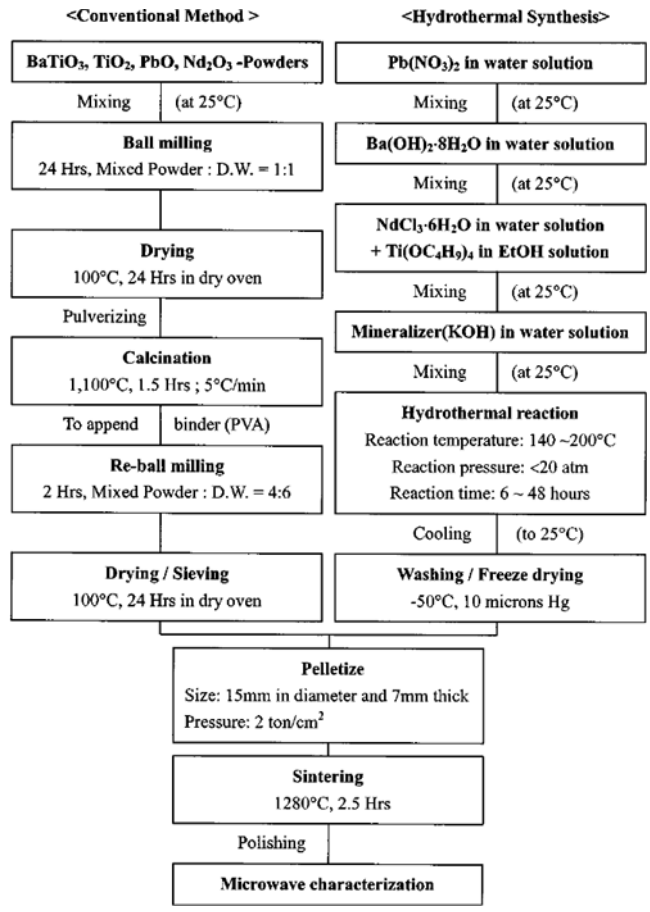

Fig. 1. Comparison of experimental procedure between conventional method and hydrothermal synthesis.

thermal methods.

1-1. Hydrothermal Method

In preparing BPNT powder, barium hydroxide [$Ba(OH)_2 \cdot 8H_2O$, Shinyo, 97%], lead nitrate [$PbNO_3$, Duksan, 99%], neodymium (III) chloride hexahydrate [$NdCl_3 \cdot 6H_2O$, Aldrich, 99.9%], titanium butoxide [$Ti(OC_4H_9)_4$, Aldrich, 97%] were used as raw materials. The feedstock solution was prepared to accommodate the molar ratio of Ba and Pb as 0.1 M, Nd as 0.4 M and Ti as 1.0 M in order to ensure the powder composition of $(Ba_{0.5}Pb_{0.5})O-Nd_2O_3-5TiO_2$. The prepared feedstock solution was put into an autoclave with the addition of a mineralizer, KOH. Reaction temperatures ranged from 140 °C to 200 °C, and reaction times ranged from 6 to 48 hrs. The mineralizer was added in amounts ranging from 1.0 M to 4.0 M. After the reaction was finished, the product was filtered and then washed with deionized water, acetic acid and ethanol, and again with deionized water successively to remove impurities. Then the synthetic product was dried in a freeze dryer [Seo and Oh, 2000].

1-2. Conventional Method

Microwave dielectric BPNT powders were also prepared by the conventional method. Commercial-grade $BaTiO_3$, TiO_2, Nd_2O_3 and PbO powders were used as the starting materials, and the formula for a result of $(Ba_{0.5}Pb_{0.5})O-Nd_2O_3-5TiO_2$ (same molar ratio of Ba and Pb) was followed. The formulated powders were ball-milled for 24 hrs in distilled water with zirconia media and dried. After that, they were calcined at 1,050 °C for 1.5 hrs with a 5 °C/min rate in the air. After organic binder (PVA 5 wt% solution) was added, the calcined powders were re-milled for 2 hrs. The mixtures were dried, pulverized and sieved.

Both the conventionally and hydrothermally prepared powders were cold-pressed into disk-shaped pellets (about 15 mm in diameter and 7 mm thick) under a pressure of 2.0 ton/cm^2. In order to remove any organic components, the pellets were heated at 550 °C for 1 hr. The pellets were sintered at 1,280 °C for 2.5 hrs with 5 °C/min rate in air.

2. Measurements

The crystallinity of the product powders was interpreted by an X-ray diffractometer (XRD: MXP3, Mac Science Co.) using a monochromatic CuK_α radiation, 40 kV, 30 mA. The morphology of the product particles was observed by using a TEM (CMS, Philips, US), and the surface morphology of the disk-shape pellet samples was observed by using an SEM (JEOL, JSM-840A). The dielectric constant (ε_r) and quality constant (Q factor) of the prepared pellets were measured at 3-4 GHz by Hakki and Coleman's method. The temperature coefficient of resonant frequency (τ_f) was found to be in the temperature range from −20 °C to 80 °C by a resonant cavity method.

RESULTS AND DISCUSSION

1. Hydrothermal Preparation of BPNT

Fig. 2 shows XRD patterns of BPNT powder prepared in a 24-hour reaction at 180 °C by hydrothermal synthesis with different concentrations of the mineralizer, KOH. Crystallite peaks of BPNT powder did not appear when the concentration of mineralizer was at 1.0 M, but we start to observe them at and above 2.0 M KOH. At 3.0 M KOH, despite the mineralizer concentration increasing, the crystallinity apparently did not improve. Therefore, the mineralizer concentration of 3.0 M was used throughout the experiments.

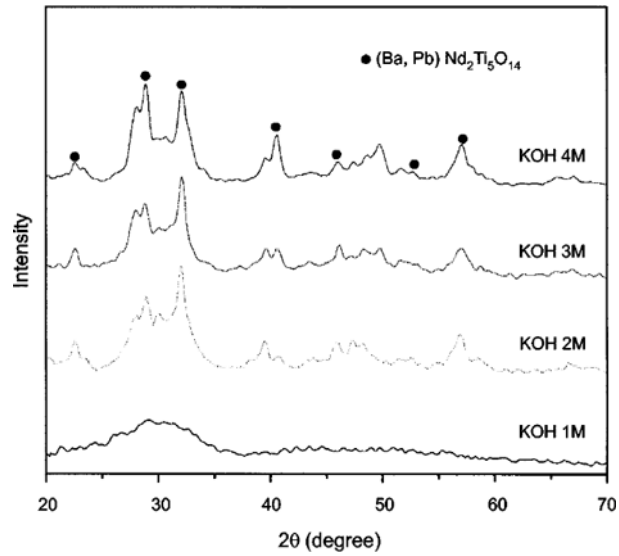

Fig. 2. XRD patterns of synthetic BPNT powder prepared with various mineralizer concentrations for a 24 hours' reaction at 180 °C.

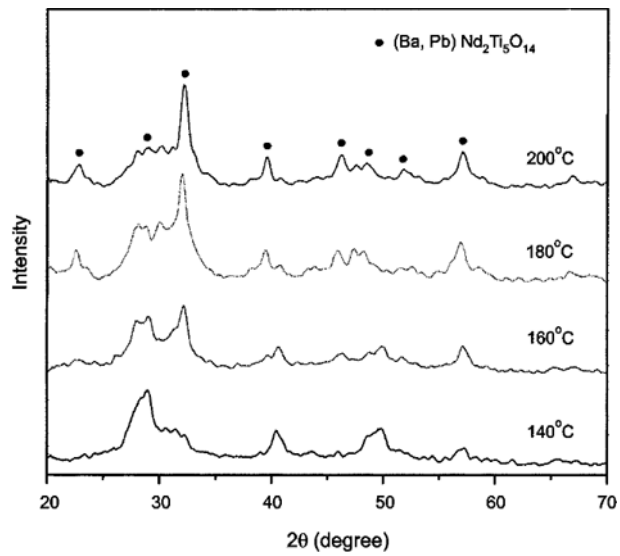

Fig. 3. XRD patterns of synthetic BPNT powder prepared at different reaction temperatures for a 24 hours' reaction with 3.0 M KOH.

Fig. 3 shows XRD patterns of BPNT powder prepared in a 24-hour reaction with 3.0 M mineralizer at different reaction temperatures from 140 °C to 200 °C. The crystallite peaks of BPNT powder were not fully developed at 140 °C, but when the reaction temperature was over 180 °C, the peaks showed better crystallinity. Therefore, we fixed the reaction temperature at 180 °C throughout the experiments.

Fig. 4 shows TEM micrographs of the synthetic BPNT powders prepared at 180 °C with 3.0 M KOH for different reaction times. With the reaction time of 12 hours, most of the particles seemed to be amorphous [Fig. 4(A)]. However, when the reaction time was 24 hours, needle-shaped crystal particles were seen [Fig. 4(B)]. Fig.

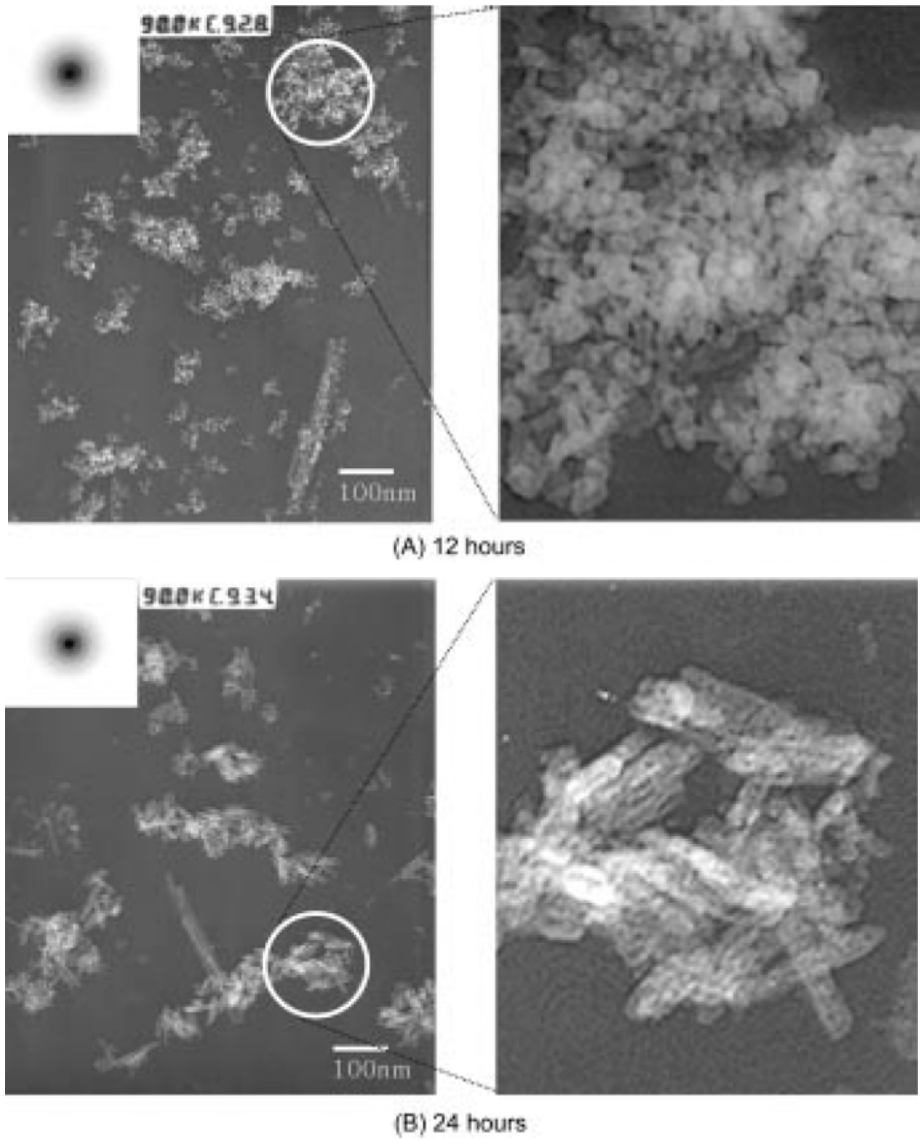

Fig. 4. TEM micrographs of synthetic BPNT powder prepared for two different reaction times, 12 and 24 hours, at 180 °C with 3.0 M KOH.

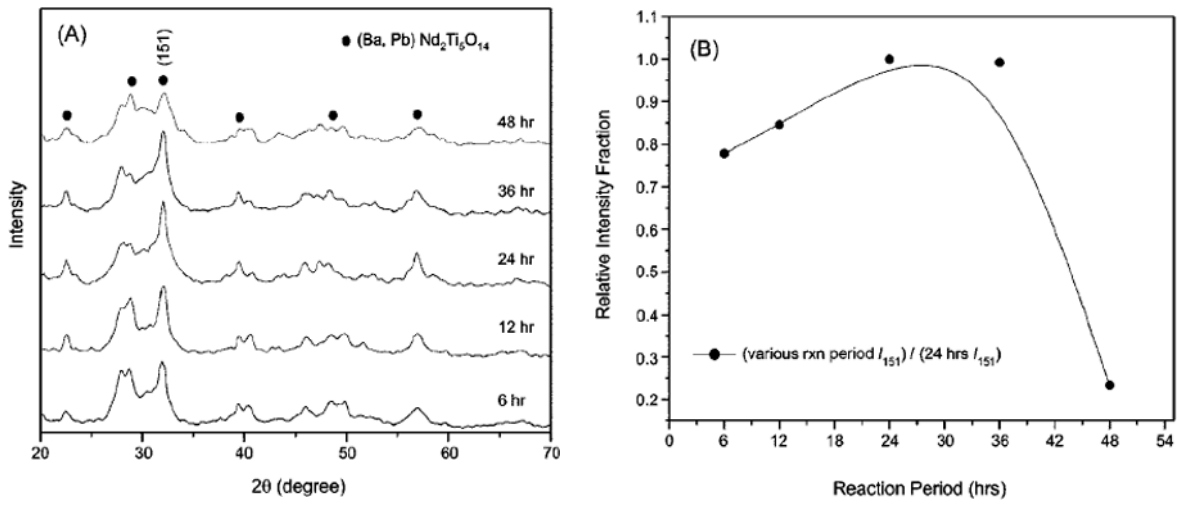

Fig. 5. XRD patterns of synthetic BPNT powder (A) and the fraction of relative intensity based on (151) face for different reaction periods with 3.0 M KOH at 180 °C.

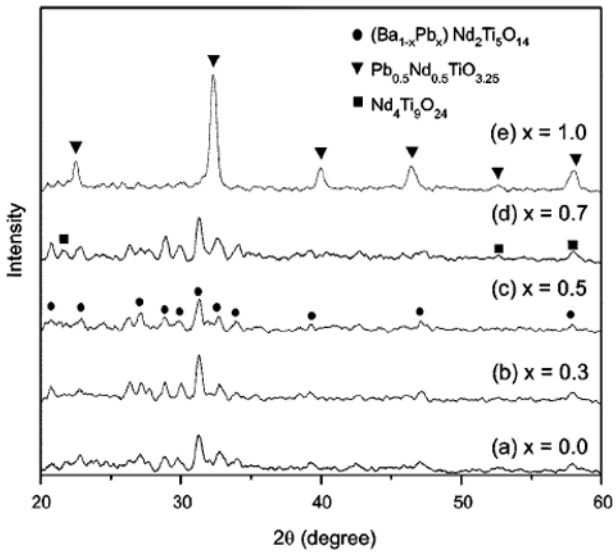

Fig. 6. XRD patterns of $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ pellets with increasing Pb addition. The pellets were prepared with hydrothermall powders sintered at 1,280 °C for 2.5 hours.

5 shows XRD patterns [Fig. 5(A)] of BPNT powders prepared with different reaction times, again using the 3.0 M concentration of mineralizer, KOH, at 180 °C. To quantify the degree of crystallization, the fraction of relative intensity [Fig. 5(B)] was calculated by using the intensity (151) peak as its basis. As shown in the figure, by increasing the reaction time, the crystallinity of the BPNT powder was enhanced, up to a 24-hour reaction time at which it was maintained. However, the intensity of the crystallite peaks decreased dramatically at reaction times over 36 hours. Therefore, the experimental conditions used throughout the experiments were a 24-hour reaction at 180 °C with 3 M KOH.

Fig. 6 shows XRD patterns of $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ pellets with increasing Pb additions. The pellets were prepared with hydrothermally synthesized powders and sintered at 1,280 °C for 2.5 hours. The crystalline phase shown in the figure is the $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ with the values of x in the range of 0.0 to 1.0. The figure shows that (Ba, Pb)O·Nd_2O_3·5TiO_2 was formed by substituting Pb for Ba in the range of 0.0 to 0.5. However, the new crystalline phase of $Nd_4Ti_9O_{24}$ or $Pb_{0.5}Nd_{0.5}TiO_{3.25}$ was weakly detected when the value of x was above x=0.7. When the mole fraction of Pb was 1.0 (x=1.0), the phase was completely transformed to new crystalline PNT, as shown in Fig. 6 [Kim and Yun, 1996]. Fig. 7 shows SEM micrographs of the above-mentioned pellets when the values of x are 0.0 (A), 0.5 (B) and 1.0 (C). As shown in the figure, the grain becomes larger and more clearly visible when the Pb mole fraction is 1.0 [Fig. 7(C)]. This figure confirms the results mentioned in the comments on Fig. 6.

Fig. 8 shows the microwave dielectric property of $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ pellets prepared with hydrothermal powders and sintered at 1,280 °C for 2.5 hours. The dielectric constant (ε_r) and quality constant (Q) were determined to be 3-4 GHz, using Hakki-Coleman's method. As the Pb mole ratio increased, the dielectric constant increased, while the Q value was maximized at x=0.5 due to an increase in the PNT phase that results in a high dielectric constant and low Q value. The temperature coefficient of the resonant frequency (τ_f) of BPNT ceramics measured by the resonant cavity method in the temperature range from −20 °C to 80 °C was made to increase with increasing Pb additions, as shown in Fig. 9. The temperature coefficient of the resonant frequency was nearly 0 ppm/°C when the Ba/Pb mole ratio was 1.0. Table 1 shows the microwave dielectric properties of BPNT ceramics with increasing Pb amounts. From the above results, shown in (Figs. 6-9), we find that the most

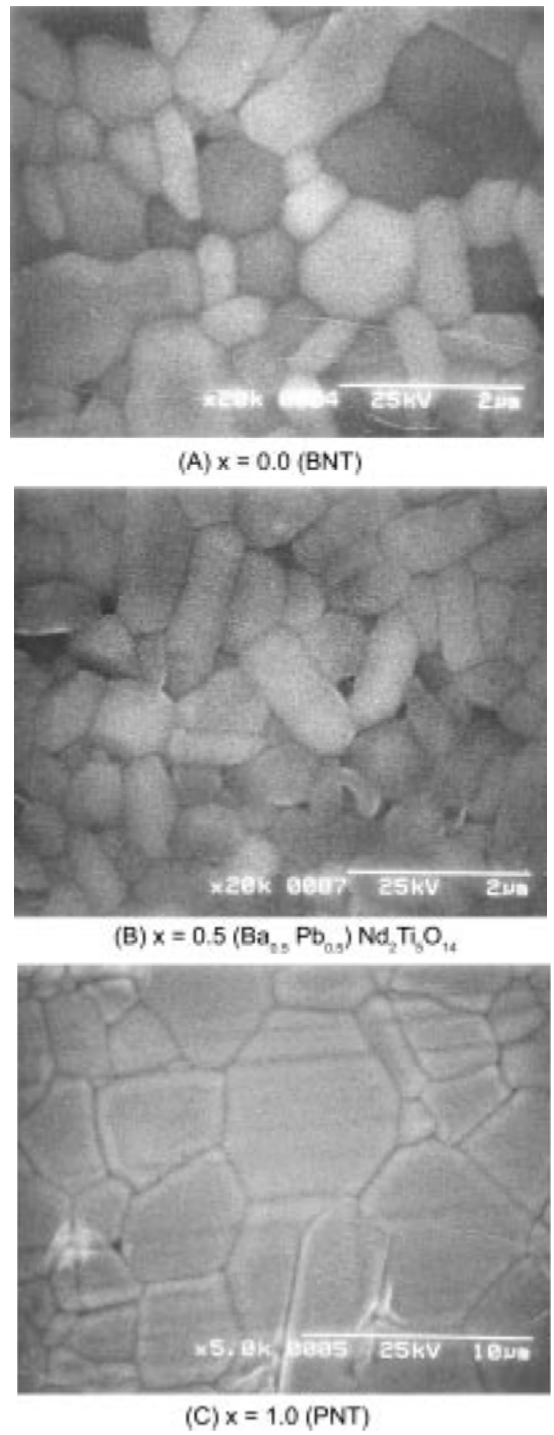

Fig. 7. SEM micrographs of $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ pellets with increasing Pb addition. The pellets were prepared with hydrothermal powders and sintered at 1,280 °C for 2.5 hours.

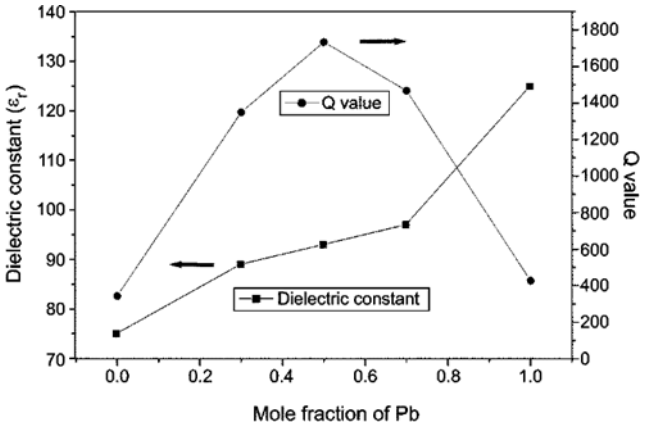

Fig. 8. The behavior of dielectric constant (ε_r) and Q value of BPNT ceramics with Pb content that prepared under optimum hydrothermal conditions and were sintered at 1,280 °C for 2.5 hours.

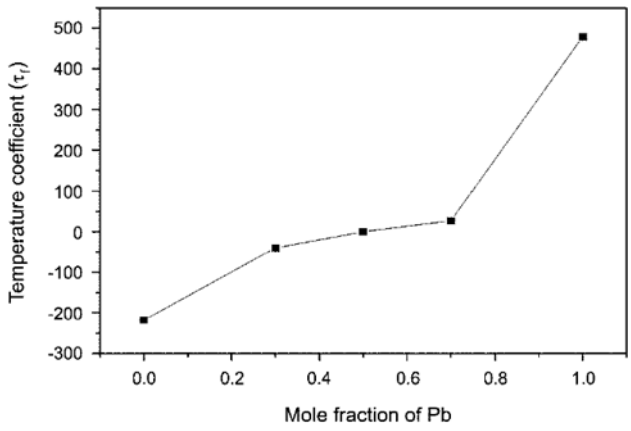

Fig. 9. The behavior of temperature coefficient of resonant frequency (τ_f) of BPNT ceramics with Pb content prepared under optimum hydrothermal conditions that were sintered at 1,280 °C for 2.5 hours.

optimum composition of $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ is obtained when x is 0.5.

2. Comparisons of Product Powders with the Conventionally Prepared Ones

Fig. 10(A) shows XRD patterns of BPNT pellets prepared with conventional and hydrothermal powders. Hydrothermal powder was prepared at 180 °C for 24-hour of reaction time and 3.0 M KOH, without calcination. Conventional powders were calcined at 1,050 °C for 1.5 hours. As shown in the figure, the XRD patterns of BPNT powder prepared by the conventional method were conspicuous. However, the crystallinity of the hydrothermally prepared BPNT powders was weak and less conspicuous than that of the conventionally prepared powders. The results in Fig. 10(A) may indicate that hydrothermally prepared BPNT powders were not fully crystallized and included some amorphous phases. These two types of powders were pressed to form pellets and sintered at 1,280 °C for 2.5 hours. Fig. 10(B) shows XRD patterns of the BPNT pellets after sintering. As shown in the figure, there was no significant difference in the crystallinity of the two types of pellets, after sintering. The crystallinity of the pellets was clearly improved after sintering,

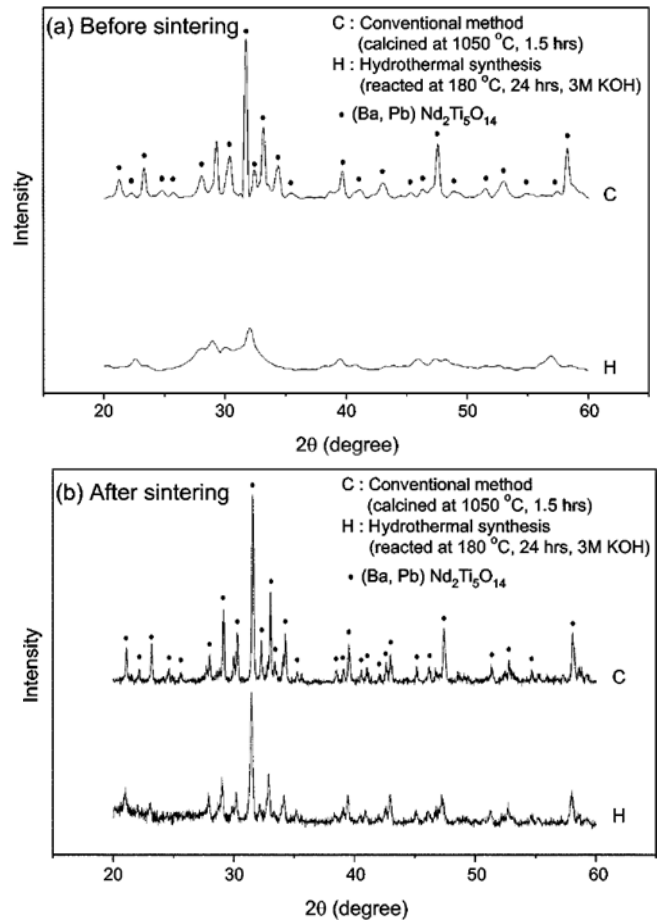

Fig. 10. XRD patterns of BPNT pellets prepared with both conventional and hydrothermal powders. The results were compared before (A) and after (B) sintering at 1,280 °C for 2.5 hours.

Table 1. Microwave dielectric properties of BaO-PbO-Nd_2O_3-TiO_2 pellets with increasing Pb addition. The pellets are prepared with hydrothermal powders

Ba/Pb mole ratio	Dielectric constant ε_r	Quality constant Q·f	Temperature coefficient of resonance frequency τ_f(ppm/°C)
$BaNd_2Ti_5O_{14}$	75	1,852	−218
$Ba_{0.7}Pb_{0.3}Nd_2Ti_5O_{14}$	89	4,721	−40
$Ba_{0.5}Pb_{0.5}Nd_2Ti_5O_{14}$	93	6,067	0
$Ba_{0.3}Pb_{0.7}Nd_2Ti_5O_{14}$	97	5,284	27
$PbNd_2Ti_5O_{14}$	125	1,494	479

a clear distinction of the crystallinity between before and after sintering for the hydrothermally prepared powders.

Table 2 shows the measured microwave dielectric properties of the pellets prepared with conventional and hydrothermal powders. The microwave dielectric properties of the pellets prepared with the hydrothermal powders were quite better than those of the pellets made with the conventional powders. We were able to guess the hydrothermally prepared powders had better uniformity of particle size and shape, with less contamination and better homogeneity in composition. From this result, we can say that hydrothermal pow-

Table 2. Comparison of microwave dielectric properties of the pellets

Powder synthesis method	Dielectric constant ε_r	Quality constant Q·f	Temperature coefficient of resonance frequency τ_f (ppm/°C)
Hydrothermal synthesis	91-93	5,834-6,067	0±1
Conventional method	89-92	4,714-4,983	7±2

ders are shown to ensure better microwave dielectric properties than conventionally mixed powders, which is essential in improving the dielectric properties while maintaining a good Q factor in the processed pellets

CONCLUSION

The hydrothermally prepared $(Ba_{0.5}Pb_{0.5})Nd_2Ti_5O_{14}$ composite powders have been analyzed and compared with conventionally prepared powders. The results are summarized as follows:

1. The optimum condition for hydrothermal synthesis of BPNT powders has been found to be a 24-hour reaction at 180 °C with 3.0 M KOH.

2. Among the hydrothermally prepared $(Ba_{1-x}Pb_x)Nd_2Ti_5O_{14}$ compositions, $(Ba_{0.5}Pb_{0.5})Nd_2Ti_5O_{14}$ powders (with a Ba/Pb mole ratio of 1.0) showed superior microwave dielectric properties. The measured microwave dielectric properties of the pellets prepared with those powders are ε_r=91-93, Q=1,667-1,744 at 3.5 GHz around and τ_f=0±1 ppm/°C, which are moderately better than those of the conventionally mixed powders.

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