

FABRICATION OF $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ CERAMICS BY FLUX-ASSISTED ULTRA-LOW SINTERING TEMPERATURE TECHNIQUE

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Abstract

$\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramic is a promising dielectric material for microwave frequencies. One of the factors that affects its dielectric properties is density, which can be controlled by fabrication processes such as sintering. Normally, conventional sintering requires high sintering temperature ($T > 1,200^\circ\text{C}$) to produce grain coarsening and pore reduction which consumes high energy. However, there has been growing interest in low-temperature ceramic processing due to its potential to revolutionize the way ceramic materials are manufactured. Cold sintering is a new sintering technique that can be used to fabricate dense ceramics below 300°C . It can be applied to a variety of compounds, and the densification process is driven by the dissolution-precipitation mechanism, with the aid of a congruent solvent, pressure, and temperature. Herein, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramics are prepared by cold sintering technique using hydrated barium hydroxide ($\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) as a flux to reduce sintering temperature and introduce densification process. The effects of processing parameters, including sintering temperature, dwelling time, pressure, and flux concentration, on the density and dielectric properties of sintered samples were investigated. Phase formation and electrical properties were characterized using X-ray diffraction (XRD), scanning electron microscopy (SEM), and an LCR meter. Under the sintering conditions $T = 150^\circ\text{C}$, pressure = 7,000 kPa, and $t = 60$ min, the obtained $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramic exhibited a relative density of $\sim 80\%$ which closes to the ceramics obtained from conventional sintering. These results suggest that sintering temperature has little influence on sample density, while applied pressure is the dominant factor in improving density. The mechanism of flux-assisted cold sintering and dielectric properties are also discussed.

Keywords: $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramic; Cold sintering; Dissolution-precipitation; Hydrated flux

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Introduction

Dielectric ceramics play a pivotal role in a vast array of modern technologies, impacting our lives in countless ways especially in communication technology, contributing to improved living standards. The dielectric properties of ceramics are of interest in the microwave frequency applications, serving as key components for resonators, filters, and antennas (Kui, 2021). The optimal performance requires dielectric materials with suitable dielectric permittivity (ϵ_r) and ultra-low dielectric loss, quantified by a high Q-factor value. Dielectric loss is related to 2 factors, (i) intrinsic and (ii) extrinsic factor. The former type depends on the interaction of phonon system while the later one relates to the ceramic imperfections (i.e. impurities, defects, and pores). Density of the sample plays a crucial role for dielectric loss adjustment which can be optimized from the ceramic processing (Silverman, 1962; Huang *et al.*, 2001).

Among the microwave dielectric compounds, perovskite-type structures show the flexibility of structural modification which facilitates property tunability. This makes them the most studied dielectric materials (Ohsato, 2016). Ba₅Nb₄O₁₅ (BNO), with its five-layer perovskite structure, has been found to be useful in the microwave applications. Its microwave dielectric properties, $\tau_f \sim +79$ ppm/°C, $Q \times f = 26,337$ GHz, and ϵ_r of 39.3 were reported by Vinies *et al.* (1996). Multiple studies demonstrate that BNO ceramic exhibits positive temperature coefficient of resonant frequency (τ_f), making it well-suited for pairing with negative τ_f materials for precise τ_f tuning (Sreemoolanadhan *et al.*, 1994; Vinies *et al.*, 1996; Kim *et al.*, 2002; Sebastian *et al.*, 2003; Kim *et al.*, 2006; Liou *et al.*, 2006; Zhuang *et al.*, 2008; Zhou *et al.*, 2010). Normally, BNO and other commercial microwave dielectric ceramics require high sintering temperature to form high density ceramics. The sintering temperature for BNO is normally above 1,400°C and must be hold at the temperature for quite long period to obtain high quality ceramics which lead to the good properties. This sintering process is the high energy and time-consuming process. Moreover, due to the effort in environmental sustainability, the aim to reduce energy consumption remains the global issue. The demand for lowering the sintering temperature for the firing process is increasing. For BNO-based ceramics, the sintering temperature can be decreased by adding a small amount of low melting temperature oxides such as B₂O₃, V₂O₅, CuO and Bi₂O₃ (Kim *et al.*, 2002; Kim *et al.*, 2003; Kim *et al.*, 2006; Jo *et al.*, 2007; Zhao *et al.*, 2007; Shigyo

et al., 2010; Lv and Zuo, 2013; Zhou *et al.*, 2021). Moreover, co-doping BNO with (W,Ti) can also minimize the sintering temperature to around 1,200°C (Zhuang *et al.*, 2008). However, the sintering temperature of the systems still shows excessively high.

Cold sintering process (CSP), one of alternative sintering techniques, has been hailed as the ultra-low sintering temperature technique ($T \leq 300^\circ\text{C}$) with an assistant of transient liquid phase and the applied pressure. The conventional sintering requires the thermally driven process for the densification while the high pressure and chemically driven process through dissolution-precipitation mechanism are the main keys for the densification in cold sintering process. Varieties of perovskite-type dielectric ceramics, such as BaTiO₃, Pb(Zr,Ti)O₃, BaZrO₃ and (K_{0.5}Na_{0.5})NbO₃, can be densified using temperature less than 300°C. However, the dielectric properties are limited due to the existence of impurity phases in some compounds which required the further thermal treatment for the property improvement. Tsuji *et al.* (2020) proposed the single step densification for BaTiO₃ ceramics using commercial BaTiO₃ (NPs) and the mixture of NaOH-KOH alkali fluxes. They successfully prepared highly dense ceramics at 300°C with the desired dielectric properties. However, the mixture of NaOH-KOH is a strong alkali with high corrosive which may lead to the harsh damage for the die. Alternatively, milder fluxes such as Ba(OH)₂·8H₂O and Sr(OH)₂·8H₂O are selected for Ba-based dielectric compounds. This kind of hydrated flux is less corrosive and can be applied for the Ba-based ceramic systems as reported by Sada *et al.* (2021a); (2021b).

In this work, we demonstrate the preparation of Ba₅Nb₄O₁₅ ceramics through cold sintering technique using Ba(OH)₂·8H₂O as a flux. The sintering temperature and the applied pressure dependence of densification are studied.

Experiment Procedures

Powder Preparation

In this study, Ba₅Nb₄O₁₅ powders were prepared by solid-state reaction. BaCO₃ (Sigma-Aldrich, >99%) and Nb₂O₅ (Aldrich, 99%) were stoichiometric mixed in ethanol and ball-milled using zirconia balls for 18 h. The resulting slurry was dried in oven overnight and then calcined at 1,200°C for 6 h with a heating rate at 5°C/min. The powder surfaces were then treated with acetic acid

to provide a thin layer of amorphous phase which facilitates the densification during cold sintering process, $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ powders were treated 1 M acetic acid with 1:5 of powder-to-acid ratio for an hour at 80°C . Subsequently, the treated powders were filtrated, washed with deionized water, and dried in oven.

Cold sintering Process

To prepare $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramics, treated $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ powders were mixed with $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (Sigma-Aldrich, >98%) with 5:1 of the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ -to- $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ ratio and ground for 2 min. The mixture was then placed into a 12 mm diameter die, covered by a heater jacket. The die was firstly heated to 80°C , hold for 30 min along with an application of pressure (3,000 kPa, 5,000 kPa, 7,000 kPa, and 10,000 kPa). Afterwards, the temperature was elevated to the desired sintering temperature ($T = 150^\circ\text{C}$, 200°C , and 250°C) and hold for 1 h, the samples were subsequently cooled down to room temperature as shown in the schematic illustration of the CSP process in Figure 1. The as-sintered ceramics were then polished and kept in the desiccator.

Sample Characterization

The experimental density ($\rho_{\text{experiment}}$) of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ pellets was calculated using the geometric method, based on their mass and volume of pellets correspond to Equation 1

$$\rho_{\text{experiment}} = \frac{m}{v} \quad (1)$$

where as $\rho_{\text{experiment}}$ is the density of pellets (g/cm^3), m is mass of the sample (g) and v is the volume of the sample (cm^3). The theoretical density ($\rho_{\text{theoretical}}$) of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ($6.42 \text{ g}/\text{cm}^3$) was calculated by using Equation 2

$$\rho_{\text{theoretical}} = \frac{nA}{V_c N_A} \quad (2)$$

whereas $\rho_{\text{theoretical}}$ is the theoretical density (g/cm^3), n is the number of the atoms per unit cell, A is the atomic weight, V_c is the volume per unit cell and N_A is Avogadro number. To calculate the relative density of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ pellets, the ratio of $\rho_{\text{experiment}}$ and $\rho_{\text{theoretical}}$ were used. For the XRD analysis, the calcined powder was finely ground, and the pellet samples were polished to a smooth surface for phase analysis. The phase formation of calcined powder and sintered sample were analyzed by X-ray diffraction (SmartLab, Rigaku, Japan) with $\text{Cu K}\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$. The diffraction data are collected at 0 - 90 degrees. The crystal structures are studied by Le Bail refinement from JANA2006 software. The surface morphology and microstructure of freshly sintered $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ were characterized by scanning electron microscopy (SEM, ZEISS, EVO MA10, Germany). Owing to the insulating feature of the ceramics, the surface was sputter-coated with a thin layer of Au. Before

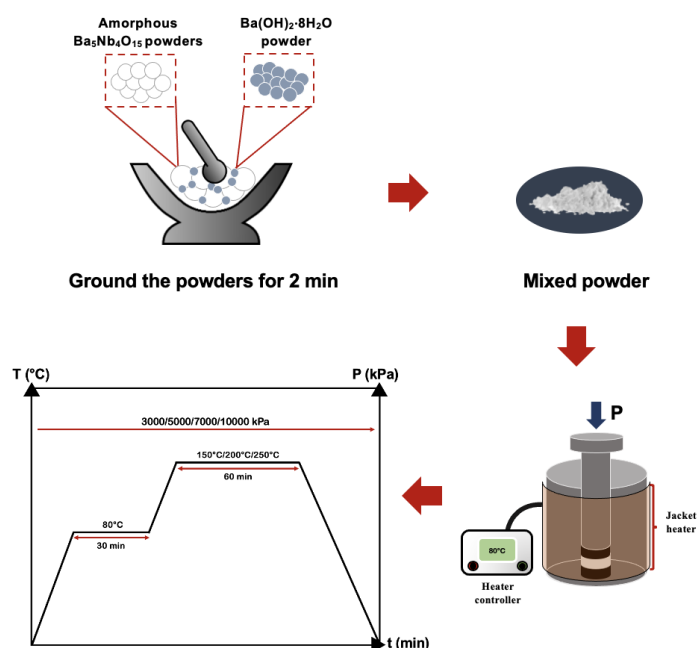


Figure 1. The schematic of cold sintering process

the dielectric feature measurement, the conducting electrodes are applied on the ceramic surfaces by using silver paint. The dielectric properties (ϵ_r) and dielectric losses ($\tan \delta$) were investigated by LCR meter (Agilent, E4908A, USA) at 100 Hz to 1 MHz from room temperature to 100°C.

Results and Discussions

X-ray diffraction patterns of calcined $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ powder is illustrated in Figure 2. A profound structural performed by Le Bail refinement using JANA2006 software confirms the trigonal symmetry with space group $p\text{-}3m1$ (Hojamberdiev *et al.*, 2016). The lattice parameters derived from the refinement are $a = b = 5.79769$, $c = 11.7773$ with R_{wp} of 13.08%. The theoretical density is calculated to be 6.29 g/cm^3 which will be used for the relative density calculation.

The as-sintered pellets show the yellowish surfaces with diameter of 12 mm and $\sim 2 \text{ mm}$ of thickness. After polishing both surfaces, the ceramics show the white surface (see Figure 3) and the measured relative density of each pellet as a function of temperature and pressure is plotted as shown in Figure 4. The effect of applied pressure is studied by the density evolution of samples. An increase in relative density for the green bodies (compacted powders at room temperature $T \sim 30^\circ\text{C}$) is observed with increasing applied pressure (3,000–10,000 kPa). This is attributed to the help of pressure

for the particle compaction. Owing to the melting point of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ powder shows at around 78°C (Tahiri *et al.*, 2003), reaction between these two precursors does not occur at this stage ($T \sim 30^\circ\text{C}$). The surface morphology of the green body obtained from scanning electron microscope, shown in Figure 5(a), illustrated the coexistence of the un-uniform particles of the precursors and pores throughout the surface. The relative densities of the green bodies are in the range of 50–57%.

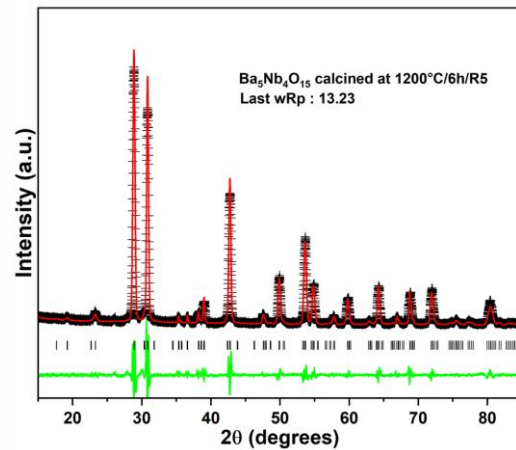


Figure 2. The x-ray diffraction pattern of the BNO powder calcined at 1200°C for 6 hours. The inset shows the crystal structure BNO derived from Vesta software

Pressure	Sintering temperature		
	150°C	200°C	250°C
3000 kPa			
5000 kPa			
7000 kPa			
10000 kPa			

Figure 3. The surface top-view images of the $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramics prepared by cold sintering process at various sintering temperatures and pressures

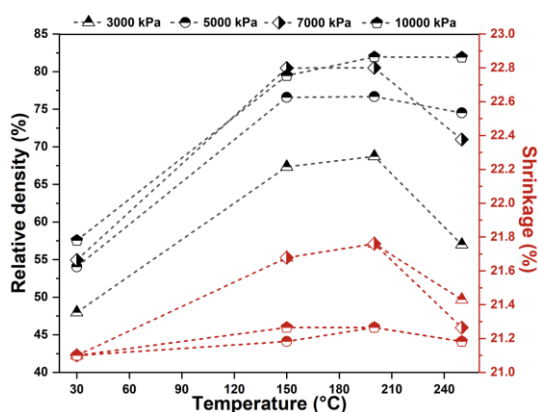


Figure 4. The relative density and shrinkage of cold-sintered samples at various temperature and pressures

The highest relative density of the green bodies is derived from the applied pressure of 10,000 kPa ($\rho \sim 57\%$). For the cold sintering process, the mixed powders were firstly heated to 80°C for 30 min together with applying pressure uniaxially. The $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ powder was melted at this stage playing a role as a flux. Afterwards, the temperature was elevated to the desired sintering temperature

(150°C, 200°C, and 250°C) and hold for an hour for the densification process. The effect of the applied pressure on the relative density of the green bodies is shown to increase as the increasing pressure. However, the similar trend is undetectable for the cold sintered samples. The samples sintered at 150°C show the improvement of relative density around 40% compare to those obtained from green bodies. A slightly increase in relative density is observed as the sintering temperature increases from 150°C to 200°C, followed by a subtle decline at 250°C. The relative density of the samples sintered at 150°C and 200°C with 7,000 kPa and 10,000 kPa applied pressures show insignificantly different. As the result, the optimum sintering condition is chosen to be $T = 150^\circ\text{C}$ at 7,000 kPa of applied pressure dwelling for an hour with the highest relative density of 80%.

The particle compaction morphology of the green body captured by light and scanning electron microscopes can be observed in Figure 5(a). The image shows the uneven particle morphology and pores with particle size around $1.74 \pm 0.82 \mu\text{m}$. The grain formation of sintered samples (Figure 5(b-c)) illustrating the surface microstructure mixed up with pores and uneven grains with the approximately grain size of $1.65 \pm 0.36 \mu\text{m}$ and

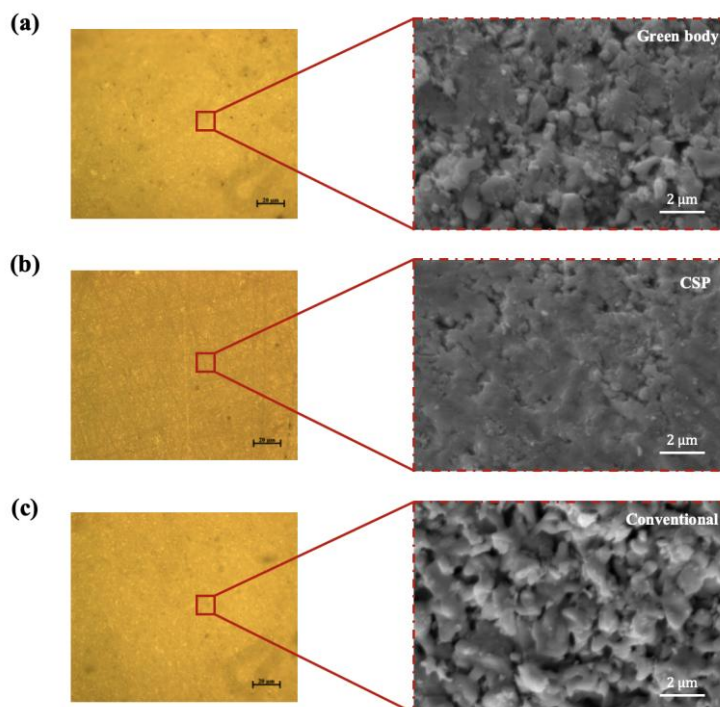


Figure 5. Surface microstructure of the (a) $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ green body, (b) cold sintered $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramic at 150°C for an hour at 7,000 kPa and (c) conventional sintered $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramic at 1,400°C captured by light and scanning electron microscopes

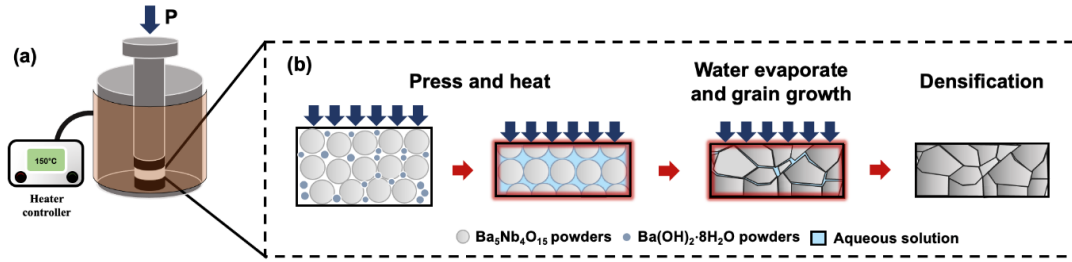


Figure 6. Schematic for densification mechanism

$2.05 \pm 0.58 \mu\text{m}$ for cold sintered and conventional sintered samples, respectively. The grains of cold sintered sample show a slightly change of grain size as compare to the initial compacted particles. However, the cold sintered morphology becomes smoother and smaller. The schematic of the densification mechanism is shown in Figure 6. As reported earlier, hydroxide fluxes facilitate the preparation of Ba-based systems (e.g., BaTiO_3) at ultra-low temperature. Besides, in Ba-based ceramics, hydroxide fluxes introduce the pressure-solution creep (dissolution→mass transport→precipitation) and thermodynamically stable which is necessary for the densification process (Liu *et al.*, 2006; Bouville and Studart, 2017; Goglio *et al.*, 2019; Ndayishimiye *et al.*, 2020). In this work, the BNO particles became coated with molten hydrated barium hydroxide flux after heating at 80°C leading to the liquid/solid interfaces between BNO and flux. At the interfaces, chemical reactions are introduced promoting the pressure solution. Under applied pressure, grain contact points experience high stress, promoting dissolution of material through reactions with the $\text{Ba}(\text{OH})_2 \cdot x\text{H}_2\text{O}$ flux. Dissolved ions migrate through the liquid phase and re-precipitate at energetically favorable sites, filling voids and leading to densification (Sada *et al.*, 2021a; 2021a; Okazaki *et al.*, 2023). Thus, the grain morphology of cold sintered sample is smoothened by this solution creep at the grain boundary interfaces. It is interestingly to note that, the BNO sample sintered by conventional sintering at $1,400^\circ\text{C}$ for 6 h shows 80% of relative density closes to those obtained from cold sintering process making it a good choice to prepare BNO ceramics. Pressure and sintering temperature are dominant factors for the process.

For the phase formation of cold sintered sample, the x-ray patterns of the mixed precursors and BNO ceramic prepared by cold sintering at 150°C are shown in Figure 7. It shows the existence of BNO pattern in either mixed precursors or as-sintered ceramics. However, the diffraction angle observed at $2\theta = 34.16^\circ$ and 44.76° for both systems

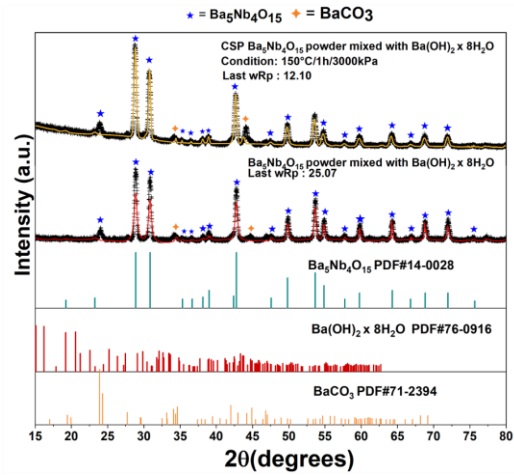


Figure 7. The X-ray diffraction pattern of the as-mixed $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ - $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and the cold sintered $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ ceramics

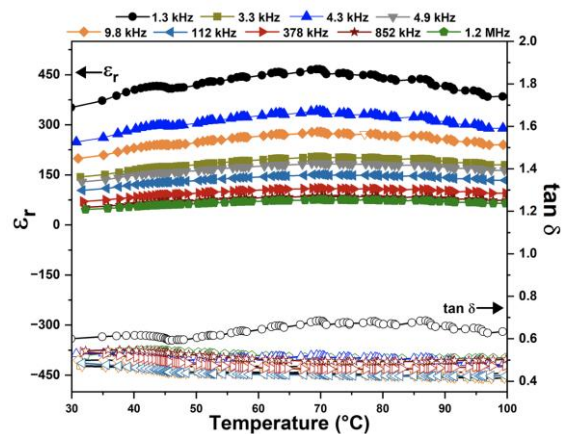


Figure 8. Dielectric properties of cold sintered sample measured at room temperature to 100°C with frequency range from 1 kHz-1.2 MHz

is possibly determined as barium carbonate peaks. The formation of barium carbonate (BaCO_3) is normally occurred due to the reaction between Ba-based hydrate flux and carbon dioxide (CO_2) in the atmosphere resulting in the formation of barium carbonate. However, it can be eliminated by the post thermal treatment.

The temperature-dependence of dielectric properties of cold sintered sample is shown in Figure 8 as a function of frequency measured at room temperature to 100°C . The ceramic shows almost temperature-independent features. The room temperature dielectric permittivity at low frequency (1 kHz) is approximately 360 with ~ 0.6 of dielectric loss. Dielectric permittivity tends to decline as the frequency rises, possibly because the dipole dynamics become hindered with increasing frequency (Cao *et al.*, 2021). The dielectric permittivity at 1.2 MHz is reported to be ~ 32 which is a little smaller than the value reported in other studies ($\epsilon_r \sim 40$) (Kim *et al.*, 2003; Zhou *et al.*, 2021). The presence and amount of BaCO_3 phase in $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ significantly impact its dielectric properties, influencing applications like capacitors, sensors, and high-frequency devices (Zu *et al.*, 2018). The main phase of BNO exhibits desirable dielectric properties, including high permittivity and low dielectric loss. When barium carbonate secondary phase arises due to impurities or processing conditions. It possesses a different crystal structure and dielectric properties compared to $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ (Tedi-Marie *et al.*, 2020). Generally, increasing BaCO_3 content leads to a decrease in permittivity. This is because BaCO_3 has a lower permittivity than $\text{Ba}_5\text{Nb}_4\text{O}_{15}$. BaCO_3 often introduces additional dielectric loss mechanisms. These can be related to interfacial polarization between the two phases, ionic conductivity in BaCO_3 , or the presence of defects. Higher BaCO_3 content typically results in increased dielectric loss.

Conclusions

In this work, the preparation of $\text{Ba}_5\text{Nb}_4\text{O}_{15}$ is demonstrated using cold sintering process. The results reveal that sintering temperature shows a slightly influence on sample density, while the applied pressure is the dominant factor for densification improvement. The optimum condition for cold sintering is $T = 150^\circ\text{C}$, $P = 7,000 \text{ kPa}$ and $t = 60 \text{ min}$ which provides 80% of relative density. The morphology studied by SEM indicates that the pressure-solution creep is possibly introduce the smoother grains of the cold sintered sample compares to the compact powders. The occurrence of barium carbonate phase in the XRD patterns

alters the dielectric properties of the sintered sample.

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