

DOI: 10.24425/amm.2020.132799

MERT GUL^{1,2*}, MEVLÜT GURBUZ³, ABDI B. GOKCEYREK⁴,
AYSEGÜL TOKTAŞ⁴, TANER KAVAS¹, AYDIN DOĞAN^{2,4}

INFLUENCE OF PARTICLE SIZE AND SINTERING TEMPERATURES ON ELECTRICAL PROPERTIES OF 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ LEAD FREE CERAMICS

In this study, lead-free 0.94 Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ (NBT-BT) compositions at morphotropic phase boundary were successfully synthesized by solid-state reaction method. The effects of the particle size for various milling time (12-24-48 hours) and sintering temperatures (1100-1125-1150-1175°C for 2h) on the electrical properties of the NBT-BT ceramics were evaluated. Experimental results showed that particle size and sintering temperatures significantly affect the electrical properties of NBT-BT ceramics. The particle size of the ceramic powders decreasing while milling time increases to 48 hours. Particle size values for 0, 12, 24 and 48 hours (h) milled powders were measured as nearly 1.5 μm, 1 μm, 700 nm, and 500 nm respectively. The bulk density enhanced with increasing sintering temperature and showed the highest value (5.73 g/cm³) at 1150°C for 48h milled powder. Similarly, the maximum piezoelectric constant (d_{33}) = 105 pC/N, electromechanical coupling coefficient (k_p) = 25.5% and dielectric constant (K^T) = 575 were measured at 1150°C for 48 h milled powder. However, mechanical quality factor (Q_m) was reduced from 350 to 175 with decreasing particle size. Similarly, remnant polarization was dropped by decreasing powder particle size from 56 μC/cm² to 45 μC/cm².

Keywords: Lead-free; NBT-BT; Particle size; Sintering; Electrical properties

1. Introduction

Lead-based perovskite structures such as lead zirconate titanate (PZT), lead magnesium niobate (PMN) and their lead titanate (PT) combinations at morphotropic phase boundary (MPB) are extensively used in transducer, sensor and actuator applications because of their advanced piezoelectric properties. However, the use of these ceramics will be restricted in the near future by environmental concerns (RoHS standards) due to their lead content. Although there have many efforts to developed new materials, the environmental friendly piezoelectric materials are still not clearly processed. The researchers are going on to contribute to replacing lead-free alternatives [1-3]. Nowadays, there is a great interest in the fabrication of sodium bismuth titanate Na_{0.5}Bi_{0.5}TiO₃ (NBT) and its barium titanate (BT) combinations which are well candidate instead of lead-based ceramics because of their satisfying piezoelectric natures such as high Curie temperature ($T_c = 320^\circ\text{C}$), large spontaneous polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) and a coercive field of $E_c = 73 \text{ kV}/\text{cm}$ [4-6]. Besides

material development, application approach towards the market has started to be launched [7]. Even though many studies concentrated on the high electrical properties of NBT-BT ceramics; their piezoelectric properties are not sufficiently superior due to their high volatilization, low densification and hard poling problem [8-10]. Therefore, a lot of studies have been published to develop electrical properties of NBT-BT by some dopants and various sintering processes. Among them, sintering temperatures and time have a critical role to perform highly dense and better electrical properties. Sintering temperatures and time directly related to particle size of the calcined powders. Decreasing particle size enhance the sintering conditions to overcome evaporation and density problems of electroceramics [11,12]. In literature, the effect of the grain size on electrical properties of sodium potassium niobate (KNN) based materials has been extensively studied. The particle size of KNN-BT after 72 h milling was reduced from 14.31 μm to 0.91 μm. It was observed that the particle size cannot be decreased in the case of ball milling over 48 hours [12]. The sintered density and electrical properties of

¹ AFYON KOCATEPE UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, AFYONKARAHISAR, TURKEY

² NANOTECH HIGH TECH CERAMICS CO., ESKİŞEHİR, TURKEY

³ ONDOKUZ MAYIS UNIVERSITY, DEPARTMENT OF MECHANICAL ENGINEERING, SAMSUN, TURKEY

⁴ ESKİŞEHİR TECHNICAL UNIVERSITY, DEPARTMENT OF MATERIALS SCIENCE AND ENGINEERING, ESKİŞEHİR, TURKEY

* Corresponding Author: mertggg@gmail.com



these ceramics were enhanced with reducing size. Ahn et al. [13] found that small particle size after 48h milling has a positive effect on the sintered density of the MnO₂ doped KNN-BT. Also, the piezoelectric constant was increased from 150 to 250 pC/N with reducing particle size. In recent years, various NBT-BT ceramic processing methods such as single crystal methods, tape casting were applied to enhance piezoelectric properties. The single crystal form of NBT-BT from is a new way to enhance piezoelectric performance. Several different processes such as Bridgman, Czochralski, flux growth, top-seeded solution growth (TSSG) and solid-state crystal growth method (SSCG) are most promising methods to improve piezoelectric properties. However, there are some disadvantageous such as a slow cooling rate, chemical inhomogeneity, high evaporation, low mass production and high production cost [14-16]. Therefore, it is essential to overcome these problems using cost-effective process. According to our knowledge, there is no detailed information about the particle size effect on sintering and electrical properties of NBT-BT ceramics.

In this work, we investigated the particle size effect on the sintering and electrical behavior of NBT-BT ceramics. The effects of the particle size for various milling time (12-24-48 h) and sintering temperatures (1100-1125-1150-1175°C for 2 h) on structural, microstructural and electrical properties of NBT-BT ceramics were investigated in detail.

2. Experimental

Na₂CO₃, Bi₂O₃, BaCO₃ and TiO₂ raw materials were mixed in the ethanol medium for 24 hours in a polyethylene bottle with the 3 mm size ZrO₂ balls. Then the mixture was dried by using rotary evaporator and calcined at 925°C for 2 h. The calcined powder was milled for 12-24-48 hours in the distilled water with wt. % 0,1 Darvan-C as the electrolyte. The particle size was measured with master sizer (Malvern Hydro 3000). After milling, the powders were dried and granulated with wt. %1 PVA added to the aqueous solution. The granulated powder was pressed into discs with a diameter of 15 mm uniaxially and cold isostatically pressed at 150 MPa in Stanfield CIP. The green pellets were sintered at 1075-1100-1125-1150-1175°C for 2h in an alumina crucible with a rising rate 5°C/min at ambient atmosphere. The density of sintered samples was measured by the Archimedes method. The morphology of the samples was observed by using Zeiss 50EVO scanning electron microscope (SEM). The crystal structure of the ceramics was analyzed with X-ray diffraction method (Rigaku Rint 2200).

For the electrical measurements, the sintered samples were ground and polished with 9 μm solution. Silver paste was coated onto the parallel surfaces and treated at 680°C for 15 minutes to obtain a good electrical contact. Specimens were poled in an oil bath at 60°C for 15 min under 6 kV/mm. The piezoelectric coefficient values were measured with d_{33} meter (Sinocera YE2730A d_{33} meter). Dielectric constant (K^T), tangent loss ($\tan\theta$) values were measured by using impedance analyzer (Agilent 4294A). Coupling coefficient (kp) values were calculated by using the

resonance-antiresonance method. Large signal measurements were done by using AixPES system at the frequency of 1 Hz based on Sawyer-Tower circuit.

3. Results and discussion

Particle size distributions have a critical role in packing density during shaping which influences the sintering. Quite large or narrow particle size is not desired to reduce the density of ceramics. Therefore, optimum particle size distributions which include both small and large particles are needed to get highly dense green and sintering temperatures [8]. Also, sintering is a diffusion related phenomena which depend on the particle size. Nanosized or submicron-sized ceramic powders have high surface energy because of their high surface area. This energy controls the sintering temperature. Therefore, reduction of the ceramic powders provides the better sintering conditions [17]. Table 1 gives the abbreviation of the milled NBT-BT powders. Figure 1 shows particle size distributions of the NBT-BT compositions for four milling times (0 h, 12 h, 24 h and 48 h). As given, they include monomodal distributions which have both small and large particles. Average particle sizes of powders were measured as 1.5 μm, 1 μm, 700 nm and 500 nm, respectively. There is a significant size difference between the samples depending on the milling time. The particle size of the 48 h milled powder was three times smaller than initial powder. Reduction of the powder to submicron size after 48 h, provides higher density and higher electrical properties of ceramics at certain sintering temperatures.

TABLE 1

Abbreviation of the NBT-BT ceramics with milling time

Composition	Milling Time (h)	Particle Size (μm)
NBT-BT	0 (initial)	1,5
NBT-BT-A	12	1
NBT-BT-B	24	0.7
NBT-BT-C	48	0.5

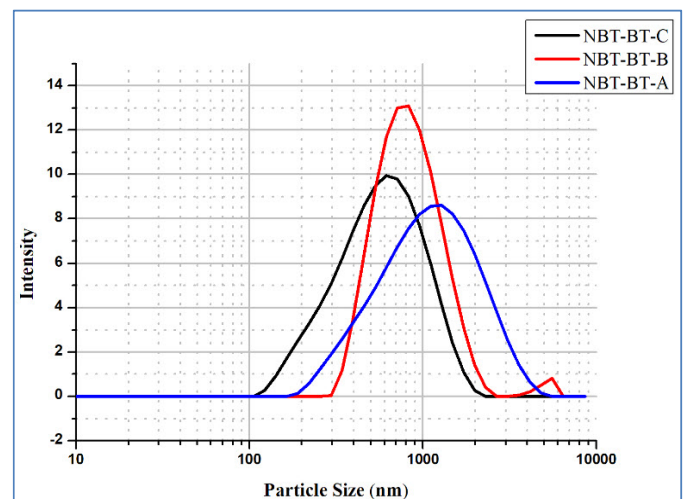


Fig. 1. Particle size distributions and average particle size of the milled NBT-BT powders

The XRD patterns of calcined and milled NBT-BT powders are shown in Figure 2a. The pure perovskite phase without undesired second phase is observed for all NBT-BT powders. The density of sintered ceramics which effect the electrical properties depends on particle size distribution, particle shape, friction between particles and mold wall, agglomeration, packing density during shaping and sintering temperature. Among them, particle size, particle shape and sintering temperature have a great effect

on density [18,19]. Figure 2b presents the density of sintered NBT-BT samples at 1075, 1100, 1125, 1150 and 1175°C for 2 hours. In general, the density increases with increasing sintering temperature and reduction of particle size. The best density (5.72 g/cm³) was observed at 1150°C for NBT-BT-C powder (48h milling). The alkaline evaporation is observed at 1175°C which reduced the density. Increasing density can be explained by Arrhenius equation (Eqn. 1) which related to diffusion and

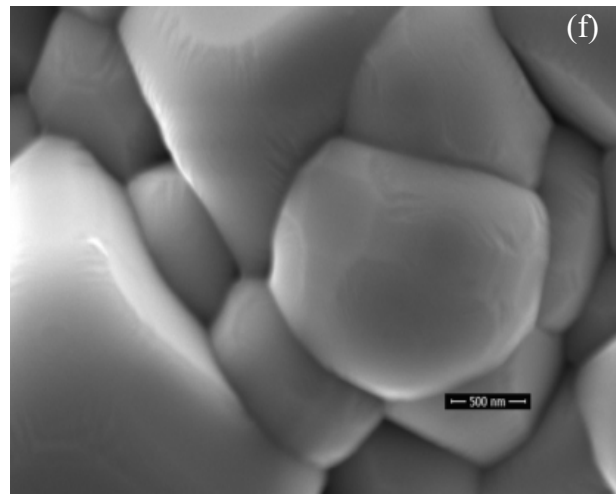
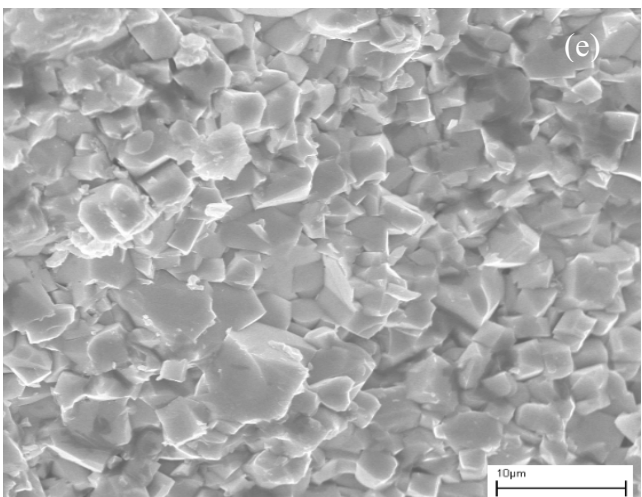
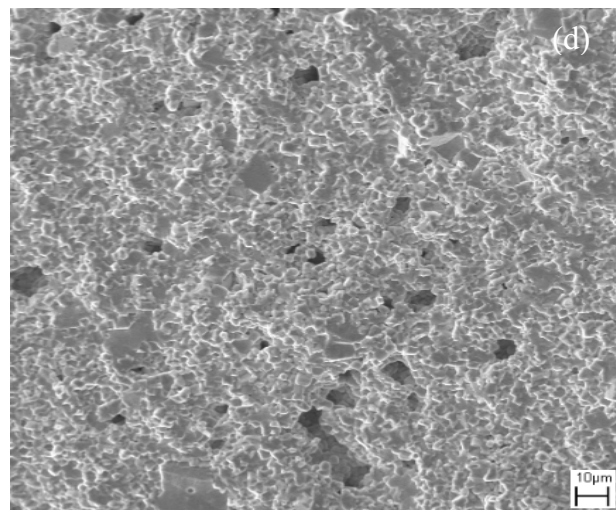
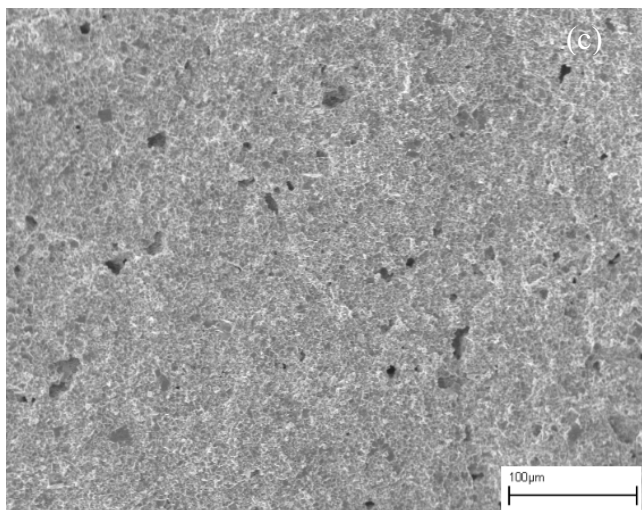
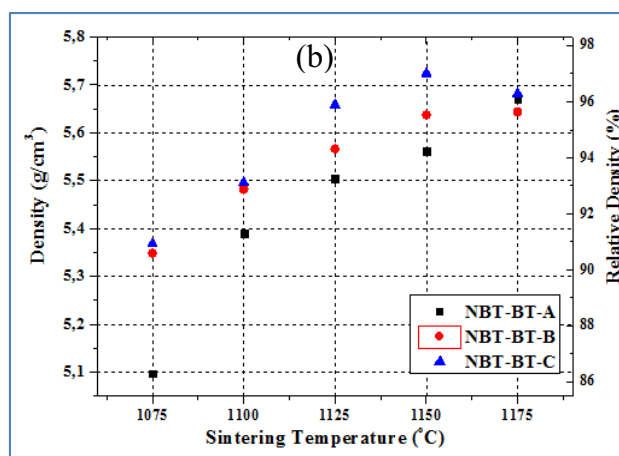
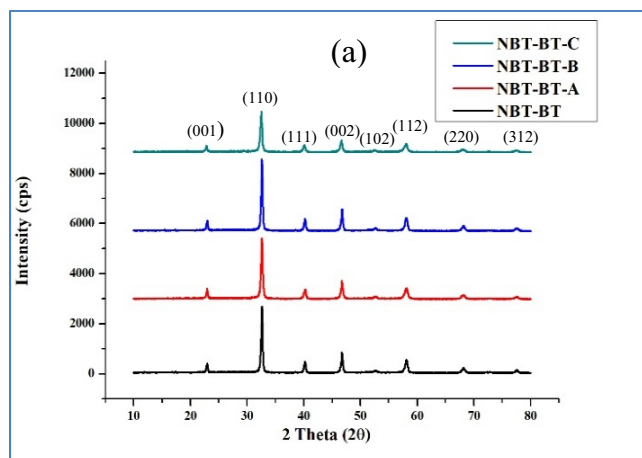


Fig. 2. XRD plot of calcined and milled powder (a), density of sintered samples for milled powders (b), low and high SEM images of sintered NBT-BT-A-B-C ceramics (c-f) 1150°C for 2h

sintering temperature. The density can be increased at higher sintering temperature due to easier atomic diffusion [18,19]. The size and shape of the particle are another control parameters to increase density. The reduction of size to submicron size level develops the sintering conditions due to the high surface area. After 48 h milling, the morphology of the powders changes to round edge cubic form which increase the packing density after shaping. It promotes more contact surface between the particles to enhance the diffusion [17].

$$D = D_0 \exp\left(\frac{-Q}{RT}\right) \quad (1)$$

where D represents the diffusion coefficient, D_0 means a constant, Q is the activation energy, R is the universal gas constant and T is the temperature.

The formation of interparticle bonding and particle necking depend on solid-state diffusion. Diffusion bonding has a critical role in microstructure and density which affects the dielectric and piezoelectric properties of the ceramics. Therefore, determination of sintering temperature has great importance to control densification, mechanical, magnetic and electrical properties of materials [18,19]. SEM images of sintered NBT-BT ceram-

ics at 1150°C for 2 hours shown in Figure 2(c-f), respectively. It is clearly shown that NBT-BT-A and NBT-BT-B have more porous microstructure than NBT-BT-C (Fig. 2(c-d)). As shown in figure, the particles consist of 3-dimensional round edge nearly 2-5 μm cubic particles. It is clearly seen that in Figure 2(e-f) the denser microstructures and good particle bonding are observed at 1150°C for NBT-BT-C powder due to easier solid state diffusion. The microstructure is developed with decreasing particle size due to its better particle packing density during shaping. It leads to more contact between the particles. This allows the atoms to move easily during sintering [17].

Figure 3a illustrates the piezoelectric properties of NBT-BT ceramics as a function sintering temperature and particle size. Generally, both the piezoelectric constant (d_{33}) and electromechanical coupling factor (k_p) shows a similar trend, developing with the increase of milling time and sintering temperatures. Especially, these properties have a maximum value at 1150°C for NBT-BT-C ceramics. The d_{33} attains a maximum value of 105 pC/N at 1150°C for NBT-BT-C ceramics. Similarly, k_p values reach to near %26 from same processing parameters. d_{33} and k_p results as a function of temperature and particle size confirm the density of ceramics. It means that low particle size and high sintering temperatures led to a high density which affects the d_{33} and k_p results positively. The highest values of the d_{33} and k_p coefficient can be explained with higher density and selected composition which is at MPB. Therefore, more dense samples includes a large number of poling directions in a MPB composition, which led to the better piezoelectric and electromechanical properties [20].

As given in Figure 4 dielectric constant of NBT-BT-C ceramics is higher due to its smaller particle size. In a small sized NBT-BT, the domain width is low and the density of the domains in the grain increases which leads to a higher dielectric constant. This is attributed to the presence of twinning granules in materials with large grain sizes [21,22]. It has been reported that the dielectric constant value increases but the values such as k_p and Q_m decrease as the particle size decreases in the range of

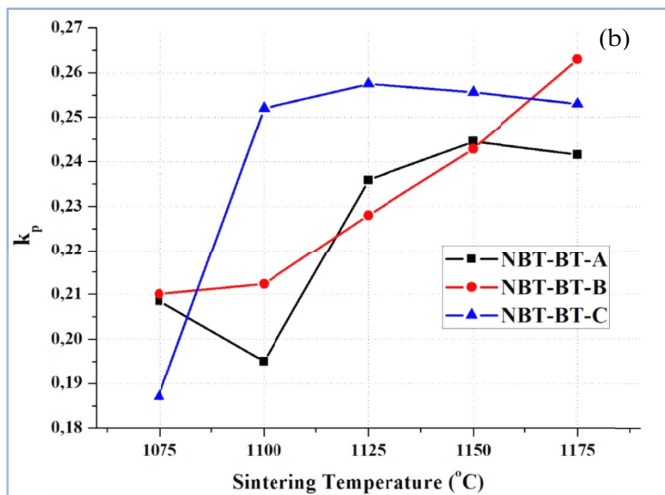
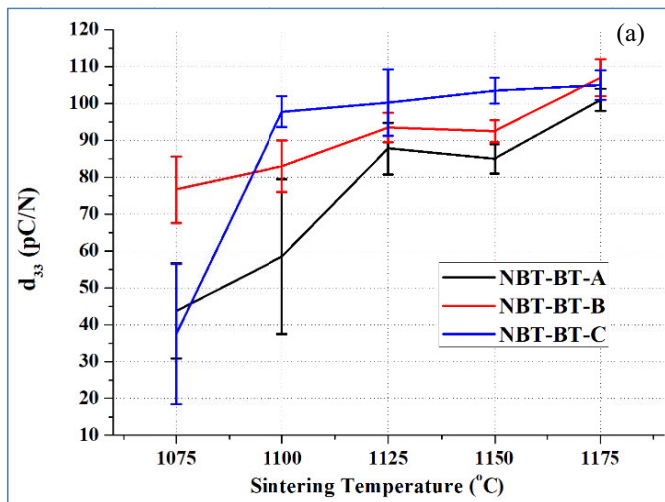


Fig. 3. d_{33} (a) and k_p (b) results of NBT-BT ceramics as a function of temperature and particle size

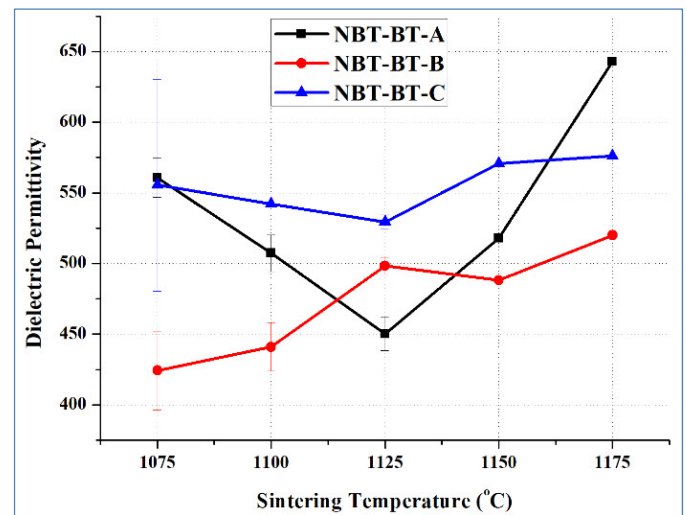


Fig. 4. Dielectric permittivity values of NBT-BT ceramics for various sintering temperatures and particle size

1-7 μm in PZT based materials. They associate with the mechanism of internal stress. In another model, as the grain size increases the dielectric constant increases. Also, reduction of grain size which leads to an increase in the volume of space charge areas [22,23].

Dielectric properties of NBT-BT ceramics depending on the frequencies are given in Table 2. The dielectric properties at room temperatures is reduced with increasing frequencies for all samples as expected. The highest dielectric constant is observed for NBT-BT-C due to its higher density.

TABLE 2

Dielectric properties of NBT-BT ceramics depending on the frequencies

Composition	100Hz	1kHz	10kHz	100kHz
NBT-BT-A	492	484	480	472
NBT-BT-B	530	520	513	509
NBT-BT-C	588	576	566	560

Although the piezoelectric and dielectric properties increase as the particle size decreases, the change in the mechanical quality factor that determines the electromechanical properties is not mentioned [12,13]. By the light of these findings, in this work,

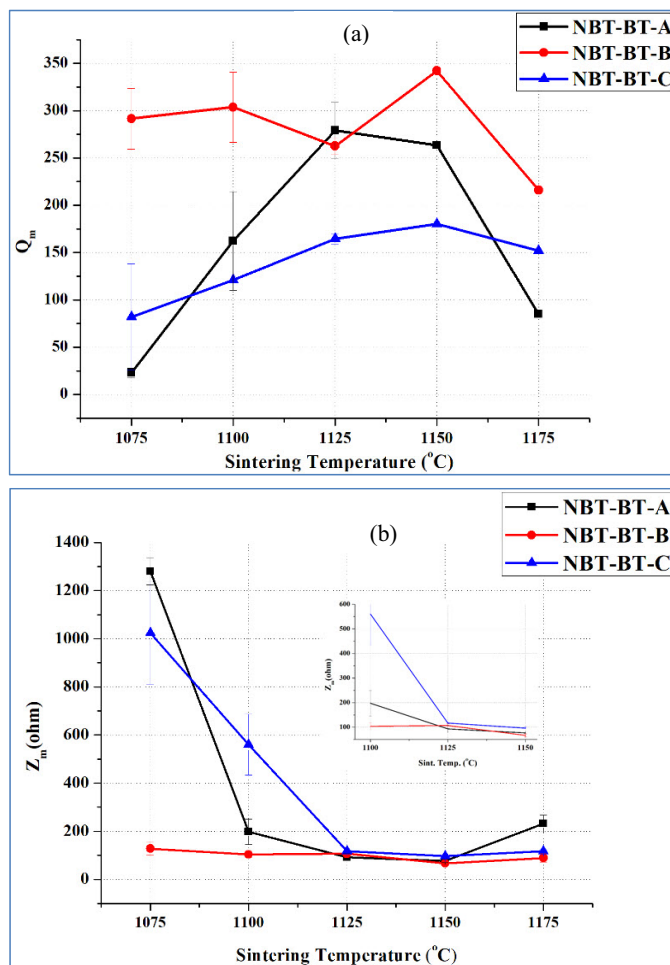


Fig. 5. Mechanical quality factor (a) and impedance values (b) of NBT-BT samples

Q_m is reduced with a smaller particle size (Fig. 5a). The relation of Q_m value to Z_m value is given by the following equation. However, the only variable is not Z_m , and the capacitance value is increased by the effect of grain size.

$$Q_m = \frac{f_a^2}{2\pi C f_r (f_a^2 - f_r^2) Z_m} \quad (2)$$

The minimum impedance values decrease as the sintering temperature approaches optimum values. Besides, the impedance value increases as the grain size decreases (Fig. 5b). The impedance value is related to grain, grain boundary and electrode impedance. Impedance value increases as the increasing particles and grain boundaries [24]. The highest impedance values in this figure are obtained in low grain size samples. Therefore the Q_m value drops too much. The Q_m value of the NBT-BT-B ceramic is higher than the NBT-BT-C composition. This is due to the more space charge fabrication, restriction of domain wall motion and the reduction of internal friction [25].

Samples with larger grain size have a higher permanent polarization value (Fig. 6). As the particle size is smaller, there are more grain boundaries in the samples for the same volume. The grain boundaries have low ferroelectricity due to irregular structures. As grain size decreases, the higher energy required to complete ferroelectric conversion. As the grain size decreases, the coercive field increases and the permanent polarization value decreases [6,26,27].

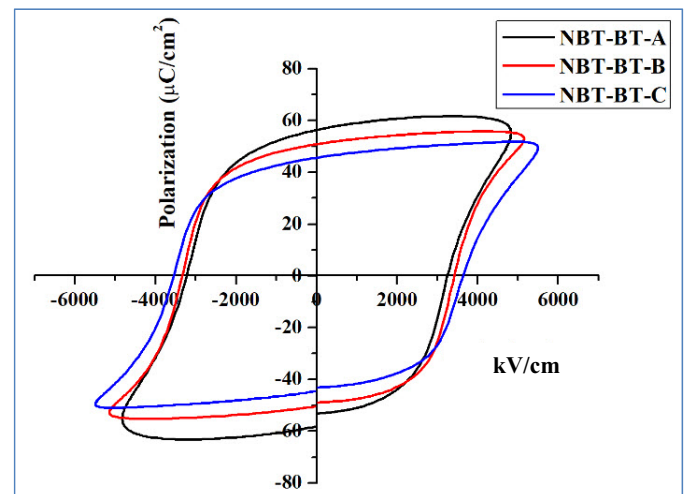


Fig. 6. Hysteresis loops of NBT-BT ceramics for various particle size and sintering temperature

The density, piezoelectric, dielectric and ferroelectric properties of the NBT-BT-C ceramics were compared with previously reported NBT-BT works which is summarized in Table 3 [20,28,29]. It can be clearly shown that that the d_{33} , k_p and P_r of NBT-BT-C ceramics in our study higher than the previous paper. Moreover, the NBT-BT-C ceramics possess the similar dielectric properties and density with published paper.

TABLE 3

The comparison of NBT-BT-C property with previously reported studies

	ρ (g/cm ³)	K^T	d_{33} (pC/N)	k_p (%)	P_r (μ C/cm ²)	E_c (kV/mm)	Q_m
[19]	5.83	—	76	16.71	23.50	4.24	—
[28]	—	601	85	—	6.03	1.40	—
[29]	—	400	40	10	—	—	—
This work	5.78	570	105	26	45	3.80	175

4. Conclusions

In this study, NBT–BT ceramics were successfully synthesized for various milling time by solid-state synthesis method. The effects of the milling time (12–24–48 h) and sintering temperatures (1075–1100–1125–1150–1175°C for 2 h) on the electrical properties of the ceramics were evaluated. From the results, both particle size and sintering temperatures significantly affect the electrical properties of the ceramics. The particle size of the ceramic powders for 0, 12, 24 and 48 h was nearly 1.5 μ m, 1 μ m, 700 nm and 500 nm, respectively. The highest density (5.73 g/cm³) was performed at 1150°C for 48 h milled powder. The maximum piezoelectric constant (d_{33}) = 105 pC/N, electromechanical coupling coefficient (k_p) = 25.5% and dielectric constant (K^T) = 575 were measured at 1150°C for 48h milled powder. However, mechanical quality factor (Q_m) was reduced with increasing milling time which was reduced from 350 to 175. The remnant polarizations was dropped by decreasing particle size. Although the piezoelectric values become higher by decreasing particle size, the optimum particle size must be found to use lead free piezoelectric materials for suitable transducer applications.

Acknowledgements

This work was supported by Science Research Projects of Anadolu University (Projects No:1705F199 and 1605F333) and Foundation of PhD Thesis Support Program in Afyon Kocatepe University in Turkey (Project No:17.FEN.BİL.71). The authors gratefully thank to Nebahat Bıyıklı for experimental supports, and following people for their supports Ali Bıyıklı, Görkem Hatipoğlu, Hakan Güleç, İrem Panta, Ayşe Korkmaz and Enes Düden. Thanks are also to Serhat Tıkız, Hakan Şahin (Afyon Kocatepe University TUAM) and Salih Akyürekli (Suleyman Demirel University) for their help in the SEM and XRD measurements. Special thanks to Assist. Prof. Dr. Metin Özgül for his valuable comments.

REFERENCES

- [1] G. Xu, Z. Duan, X. Wang, D. Yang, J. Cryst. Growth **275** (1-2), 113-119 (2005).
- [2] X. Yi, H. Chen, W. Cao, M. Zhao, D. Yang, G. Ma, C. Yang, J. Han, J. Cryst. Growth **281** (2-4), 364-369 (2005).
- [3] P. Li, B. Liu, B. Shen, J. Zhai, L. Li, H. Zeng, Ceram. Int. **43**, 1008-1021 (2017).
- [4] R.F. Ge, Z.H. Zhao, S.F. Duan, X.Y. Kang, Y.K. Lv, D.S. Yin, Y. Dai, J. Alloy Compd. **724**, 1000-1006 (2017).
- [5] T. Takenaka T., K.I. Maruyama, K. Sakata, Jpn. J. Appl. Phys. **30**, 2236-2239 (1991).
- [6] C.A. Randall, N. Kim, J.P. Kucera, W. Cao, T.R. Shrout, J. Am. Ceram. Soc. **81**, 677-688 (1998).
- [7] J. Rödel, K.G. Webber, R. Dittmer, W. Jo, M. Kimura, D. Damjanovic, J. Eur. Ceram. Soc. **35** (6), 1659-1681 (2015).
- [8] W. Ge, H. Liu, X. Zhao, X. Pan, T. He, D. Lin, H. Xu, H. Luo, J. Alloy Compd. **456** (1-2), 503-507 (2008).
- [9] Q. Xu, S. Wu, S. Chen, W. Chen, J. Lee, J. Zhou, H. Sun, Y. Li, Mater. Res. Bull. **40** (2), 373-382 (2005).
- [10] J. Suchaniez, B. Glos, G. Stopa, T. Kruzina, J. Kusz, M. Zubka, W. Hofmeister, I.J. Sumara, D. Wcislo, K. Pytel, M. Dambekalne, A. Sternberg, Integr. Ferroelectr. **108**, 98-105 (2009).
- [11] S. Hamdelou, K.L. Guergouri, Arab. Appl. Nanosci. **5** (7), 817-825 (2015).
- [12] S.G. Bae, H.G. Shin, K.H. Chung, J.H. Yoo, I.H. Im, Trans. Electr. Electron. Mater. **16** (4), 179 (2015).
- [13] C.W. Ahn, S. Nahm, M.J. Yoo, H.G. Lee, S. Priya, J. Mater. Sci. **43** (17), 6016-6019 (2008).
- [14] S.R. Kanuru, K. Baskar, R. Dhanasekaran, B. Kumar, J. Cryst. Growth **441**, 64-70 (2016).
- [15] K.S. Moon, D. Rout, H.Y. Lee, S.L. Kang, J. Cryst. Growth **317** (1), 28-31 (2011).
- [16] X. Li, C. Chen, H. Deng, H. Zhang, D. Lin, X. Zhao, H. Luo, Crystals **5** (2), 172-192 (2015).
- [17] G. Günkaya, M. Gürbüz, A. Doğan, J. Sensors 971473, 9 pages (2015).
- [18] M. Rahimian, N. Ehsani, N. Parvin, H.R. Baharvandi, J. Mater. Process Tech. **209** (14), 5387-5393 (2009).
- [19] MA Bhuiyan, SM Hoque, S. Choudhury, J. Bangladesh Acad. Sci. **34**, 189-195 (2010).
- [20] S. Swain, S. K. Kar, P. Kumar, Ceram. Int. **41** (9), 10710-10717 (2015).
- [21] G. Arlt, Ferroelectrics **104** (1), 217-227 (1990).
- [22] N. Kim. Grain size effect on the dielectric and piezoelectric properties in compositions which are near the morphotropic phase boundary of Lead Zirconate-Titanate based ceramics. PhD thesis. The Pennsylvania State University, Pennsylvania, PA 16802 (May).
- [23] K. Okazaki, K. Nagata, J. Soc. Mat. Sci. Jpn, **4**, 404 (1972).
- [24] R. Selvamani, G. Singh, V.S. Tiwari, Mater. Res. Express **3** (5), 056301 (2016).
- [25] S. Takahashi, M. Takahashi, Jpn. J. Appl. Phys. **11**, 31 (1972).
- [26] V.R. Mudinepalli, L. Feng, W.C. Lin, B.S. Murty, J. Adv. Ceram. **4** (1), 46-53 (2015).
- [27] B.M. Jin, J. Kim, S.C. Kim, Appl. Phys. A **65** (1), 53-56 (1997).
- [28] S.R. Kanuru, K. Baskar, R. Dhanasekaran, Ceram. Int. **42** (5), 6054-6064 (2016).
- [29] J.H. Cho, Y.H. Jeong, J.H. Nam, J.S. Yun, Y.J. Park, Ceram. Int. **40** (6), 8419-8425 (2014).