Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 871–877

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Microwave-assisted synthesis and sintering of potassium sodium niobate lead-free piezoelectric ceramics

Mahdi Feizpour*, Hadi Barzegar Bafrooei, Roghayeh Hayati, Touradj Ebadzadeh

Materials and Energy Research Center, P.O. Box: 14155-4777, Tehran, Iran

Received 18 April 2013; received in revised form 22 June 2013; accepted 22 June 2013
Available online 28 June 2013

Abstract

Synthesis and sintering of (K,Na)NbO_3 lead-free piezoelectric ceramics (KNN) were carried out using conventional and microwave heating processes. Microwave calcination resulted in the formation of single-phase orthorhombic perovskite structure by heating up to 950 °C. Characterization of synthesized powders with FTIR, XRD and DSC techniques revealed that without soaking time and in spite of the very short heating time in microwave, the powder calcined at 950 °C has all physical properties similar to powder synthesized in conventional furnace at the same temperature with a step by step heating regime. The bulk density of 93.8 %, piezoelectric charge coefficient (d_{33}) of 85 pC/N and remnant polarization (P_r) of 18 μC/cm^2 were achieved for sample sintered in microwave furnace at 1115 °C. These values are satisfactorily comparable with corresponding values of conventional sintering. Results showed that the microwave heating is a promising method in calcination, synthesis and sintering of potassium sodium niobate lead-free piezoelectric ceramics.

© 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: A. Microwave processing; A. Calcination; A. Sintering; C. Piezoelectric properties; Potassium sodium niobate

1. Introduction

PZT and other lead-based ferroelectrics are widely used because of their excellent piezoelectric properties. Due to toxicity of lead oxide and its harmful effects on environment and human beings, many efforts are done to find alternative safe materials. Among the lead-free piezoelectric compositions, potassium sodium niobate ((K,Na)NbO_3:KNN) is considered to be promising to replace PZT, due to its high curie temperature and relatively strong piezoelectricity. However, the volatility of Na and K at elevated temperature and the sensitivity of the compound to the moisture make it difficult to obtain dense and well-sintered KNN ceramic by conventional sintering [1–4].

Several powder synthesis methods are studied to synthesize KNN powder. Methods such as solid state reaction [5,6], sol–gel [7,8], hydrothermal/microwave-hydrothermal [9,10] and mechanochemical activation [11,12] have been studied in details and in some cases shown a good powder characteristic in the terms of subsequent shaping and sintering process and electrical properties. Besides, many techniques are utilized and expanded for sintering of KNN ceramics such as normal and pressureless sintering [13,14], hot pressing [15,16], spark plasma sintering [17,18]. Additionally, sinter aids and additives [19,20] are studied in undoped KNN and doped with some isovalent cations like Li^+, Ta^{5+} and Sb^{5+}. However, all above synthesis and sintering methods are costly, require prolonged processing time and have relatively low efficiency.

Microwave heating is a process in which the material absorbs the electromagnetic energy volumetrically and transforms it into the heat by coupling with microwave radiation. This is fundamentally different from conventional methods where heat is transferred through the material by the mechanisms of conduction, radiation and convection. In conventional heating, since the surface of the material is first heated, there is a temperature gradient from the surface to the inside, while microwave heating generates heat within the material first and then heats the entire volume. The specificities and the interests of microwave process are (i) heating rates induced up to

---

*Corresponding author. Tel.: +98 26 36204131; fax: +98 26 36204139.
E-mail address: iusteng@gmail.com (M. Feizpour).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.06.081

several degrees per second, (ii) core heating and (iii) energy utilization efficiency of 80–90%. Furthermore, it is a very clean and non-polluting method and results in better reaction yields [21,22].

Compared with conventional methods, a dense body with improved microstructure can be obtained by microwave heating in a much shorter time. Many papers have reported the effect of microwave heating on the synthesis and sintering of ceramic materials [23,24] and electroceramics [25,26]. In the present work, the effect of microwave heating on calcination process and synthesis of the stoichiometric compound of $(K_{0.5}Na_{0.5})NbO_3$ from carbonate-based raw materials were considered and well characterized. Also, the sintering of KNN ceramic using microwave heating was investigated and compared with conventional heating process.

2. Materials and methods

The raw materials were Na_2CO_3 and K_2CO_3 ($\geq$ 99% purity, Sigma-Aldrich), and Nb_2O_5 ($\geq$ 99.9% purity, Sigma-Aldrich). The powders were dried at 220 °C for 12 h and weighted carefully based on stoichiometric undoped KNN ($(K_{0.5}Na_{0.5})NbO_3$) formulation and were mixed for 6 h using zirconia balls in a polyethylene jar with ethanol as medium. After drying the slurry using hotplate-stirrer, the obtained powders were sieved and calcined at 950 °C in conventional furnace and at 350 −950 °C in microwave furnace. The step by step heating regime of conventional furnace was based on the results of Nagata et al. [27] and our previous work [28] in which the stoichiometric mixture of powders were heated in furnace with the rate of 2 °C/min and were held isothermally at temperatures of 600, 850 and 950 °C for 3, 5 and 2 h, respectively. A schematic diagram of this step by step heating regime is shown in Fig. 1.

On the other hand, to investigate the microwave synthesis process, the initial mixed powders were heated at different temperatures from 350 °C to 950 °C in microwave furnace. The arrangement of microwave system was based on our previous setup [24] in which SiC crucible was used as susceptor and temperature was measured accurately by an optical pyrometer (RAYR312MSCL2G) focused through a hole in the top of insulation on the surface of the sample. The average heating rate was ~30 °C/min.

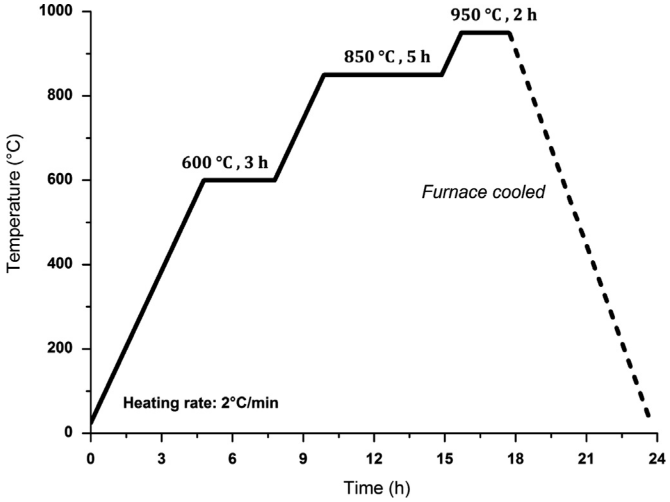

Fig. 1. The heating regime of step by step calcination process in conventional furnace.

To characterize and compare the heat treated powders, X-Ray Diffraction (XRD, Siemens, D-500 system), Fourier Transform Infra Red spectroscopy (FTIR, Bruker, V33 spectrophotometer) and Differential Scanning Calorimetry (DSC, DSC1, Mettler Toledo) were used. Cu–Kα monochromatized radiation source with Ni filter were used for XRD in the range $2\theta = 10–80°$. FTIR spectroscopy was carried out from 400 to 4000 cm^{-1}, using KBr pellets containing 1 wt% sample in KBr. DSC measurement was carried out in the temperature range of 25–500 °C at a heating rate of 5 °C/min under argon atmosphere and was used to evaluate the transformation from ferroelectric–orthorhombic to ferroelectric–tetragonal and from ferroelectric–tetragonal to paraelectric–cubic of KNN powders synthesized in conventional and microwave furnaces.

Particle Size Analyzer (PSA, Fritsch Particle Sizer, analysette 22), Gas Pycnometry (Micromeritics, AccuPyc 1330) and BET techniques (Micromeritics, Gemini 2375) were also used to measure the physical properties of powders such as particle size distribution, powder density and specific surface area, respectively. The morphology of the powders and microstructure of sintered samples were investigated by using a Philips Scanning Electron Microscope (SEM) operating at 20 kV.

In order to study and compare two different sintering routes, the conventionally-synthesized KNN powder was uniaxially pressed at 70 MPa into disks of 10 mm diameter and ~1.5 mm thickness. Sintering was carried out at 1115 °C for both conventional and microwave heating processes. The bulk density was measured by the Archimedes method. At least three samples were used for every measurement and mean value was reported. Samples were polished and electroded with silver paste. Using a precision LCR-meter model LCR8110G (GWinsteck, Taiwan), the relative dielectric constant (ε_r), dissipation factor (tan δ) and the temperature dependence of dielectric constant from room temperature to 550 °C were measured at 1 kHz. The d_{33} piezoelectric charge coefficient was measured one day after poling under a field level of 4 kV/mm for 30 min at 120 °C by means of a Pennebaker model 8000 piezo d_{33} tester (APC Inc., USA). *P–E* hysteresis loops were evaluated at room temperature under 5 kV/mm AC field at 50 Hz with a test unit based on modified Sawyer-Tower circuit.

3. Results and discussion

FTIR spectra of initial mixed powder and the powders heated in microwave furnace from 350 °C to 950 °C are shown in Fig. 2. The peaks in the range of 1000–2000 cm^{-1} were related to CO_2 (wavenumber of 1430 cm^{-1}) and adsorbed water (wavenumber of 1630 cm^{-1}) vibrations. The broad peak in the vicinity of 3450 cm^{-1} is related to the stretching of H_2O [8,29]. The maximum absorbance belongs to the bending vibrations of carbonate groups in the stoichiometric mixture of raw powders.

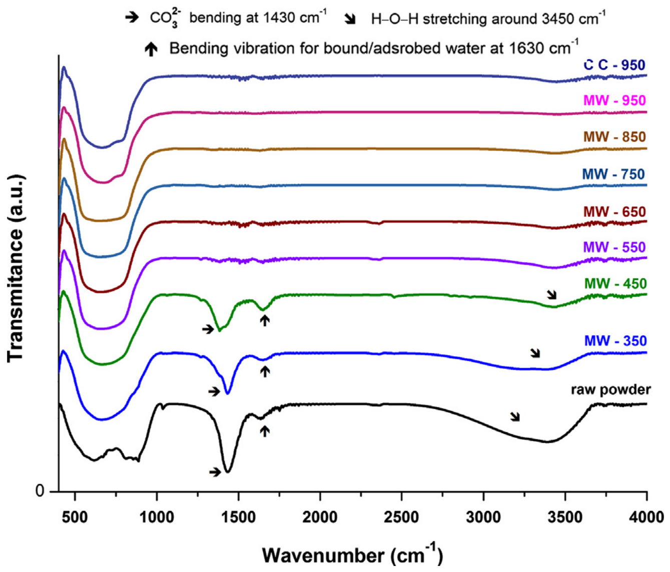

Fig. 2. FTIR spectra of initial mixed powder (raw powder), powders heated in microwave furnace (MW) from 350 °C to 950 °C and in the conventional furnace at 950 °C (CC-950).

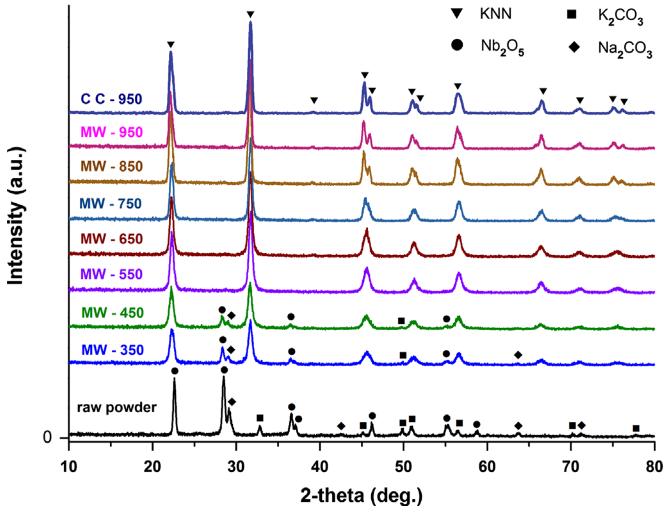

Fig. 3. XRD patterns of initial mixed powder (raw powder), powders heated in microwave furnace (MW) from 350 °C to 950 °C and powder synthesized in conventional furnace at 950 °C (CC-950).

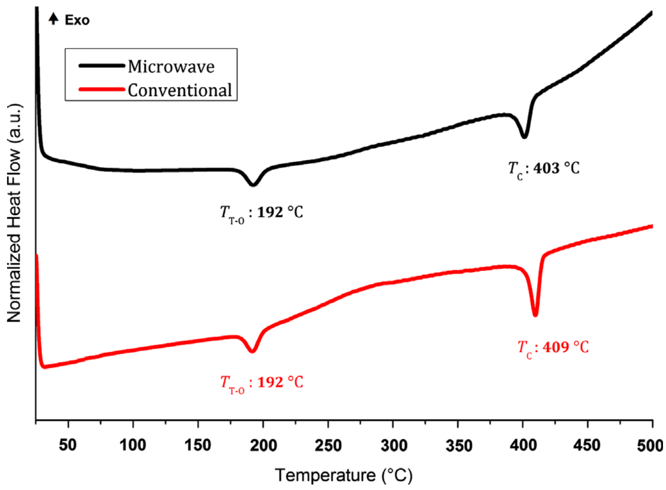

Fig. 4. DSC curves of KNN calcined powders at 950 °C in conventional and microwave furnaces.

By increasing the calcination temperature to 550 °C, this peak disappeared and further increase in temperature up to 950 °C did not considerably affect the FTIR spectra. FTIR spectrum of conventionally synthesized KNN using step by step calcination process is also shown in Fig. 2. It is seen that the synthesized powders of both conventional and microwave heating at 950 °C have similar FTIR spectra, specially at wavenumbers less than 1000 cm^{-1} which are known as characteristic peaks of material and are related to the Nb–O octahedral vibrations which is a sign of the formation of perovskite structure [30,31].

The X-ray diffraction patterns of the KNN raw powders and the powders heated in microwave furnace at 350–950 °C are shown in Fig. 3. The main peaks of starting raw materials are observed at XRD pattern of mixed powders (raw powder) before heat treatment. Increasing the microwave heating temperature to 550 °C leads to the disappearance of these peaks and the formation of perovskite KNN (PDF card number 32-0822). A further increase in the calcination temperature from 750 °C to 950 °C leads to the splitting of some peaks, specially at $2\theta = 45\text{–}47^\circ$ and 51–53°, which indicates the formation of single phase orthorhombic perovskite KNN at 950 °C in microwave furnace [32]. The XRD pattern of KNN powder heated conventionally at 950 °C (CC-950) is also shown in Fig. 3. As Fig. 3 reveals, there is no significant difference between XRD patterns of conventionally and microwave heated KNN powders at 950 °C.

XRD and FTIR results revealed that the orthorhombic perovskite KNN phase synthesized at 950 °C in microwave and conventional furnaces have the same characteristics. It is worth to mention that the formation of single phase KNN in conventional furnace needs about 18 h, while it only takes around 31 min in microwave furnace without soaking time.

In order to further verify the characteristic of powders with different heating processes, DSC analysis of powders calcined in conventional and microwave furnaces were performed and depicted in Fig. 4. Two endothermic peaks observed in each graph correspond to the respective phase transitions, i.e., Tetragonal to Orthorhombic (T_{T-O}) and the Curie temperature (T_C) [33]. According to Egerton and Dillon [34], these temperatures are nominally 220 °C and 420 °C, respectively. Fig. 4 shows nearly the same thermal behavior of powders with different synthesis methods. Both curves have the same T_{T-O} (192 °C). T_C of microwave calcined powder is 403 °C which is close to that of conventional calcination, 409 °C. However, the lower T_C of microwave calcined powder may be attributed to the lower grain size [35].

The SEM micrographs of the powders calcined at 950 °C via conventional and 550–950 °C via microwave heating are shown in Fig. 5. Fig. 5(a)–(e) indicates that the particle size increases slightly as the calcination temperature increases. The morphological investigations revealed the presence of cuboid

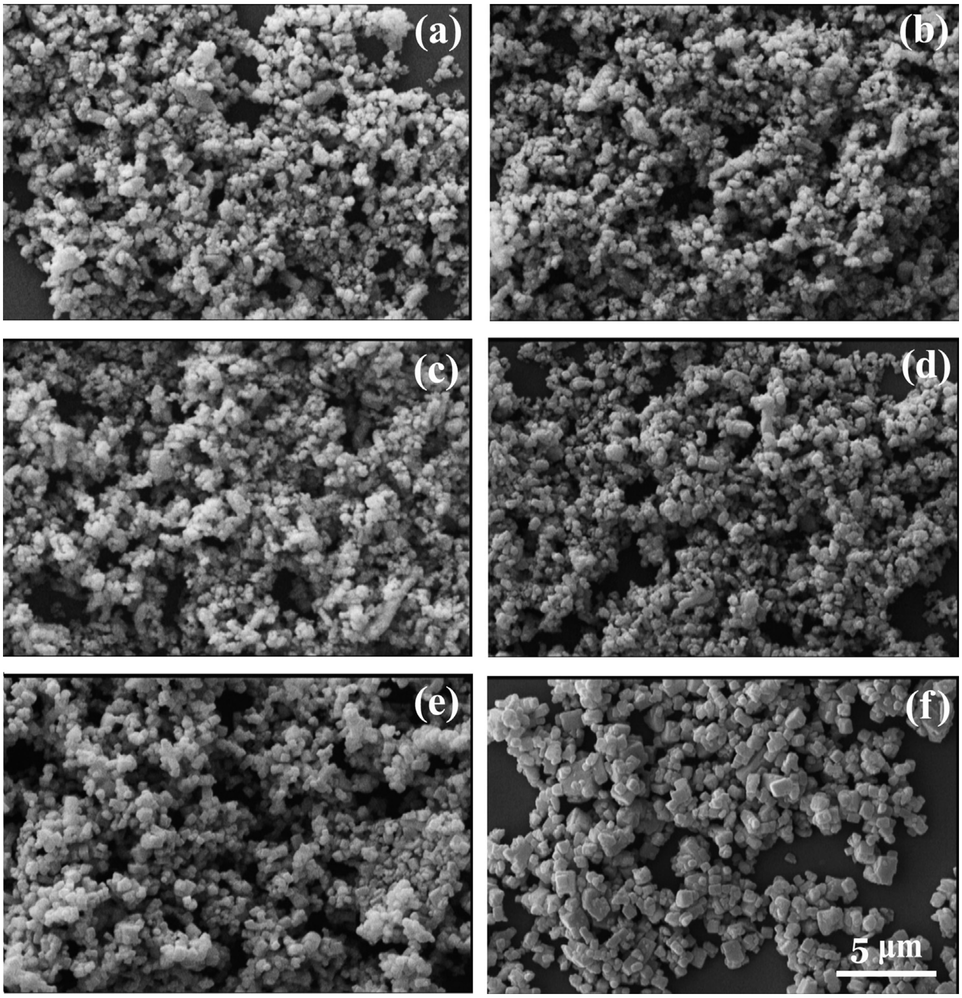

Fig. 5. SEM images of KNN powders of two different calcination routes: microwave heating at (a) 550 °C, (b) 650 °C, (c) 750 °C, (d) 850 °C, (e) 950 °C and (f) conventional calcination at 950 °C. (All images have the same magnification, 5000 × .)

grains of about 0.6 μm (Fig. 5(e)) and 1.1 μm (Fig. 5(f)), estimated by the linear intercept method, for powders synthesized in microwave and conventional furnaces at 950 °C, respectively.

Physical properties of powders such as powder density, particle shape, particle size distribution and specific surface area of powders calcined via these two heating methods are summarized in Table 1. It is seen that both heating processes lead to powders with nearly the same characteristic. However, the powder heated in microwave at 950 °C has finer particles and narrower distribution than that heated in conventional furnace at the same temperature.

To evaluate the microwave-assisted sintering of KNN ceramic, the conventionally synthesized powder was pelletized and sintered at 1115 °C in both conventional (with a heating rate of 5 °C/min and soaking time of 2 h [36]) and microwave (total heating time of 36 min without soaking time) furnaces. Fig. 6 shows the SEM images of the fracture surface of KNN samples sintered in (a) conventional and (b) microwave furnaces. As it is observed, the cuboid grains sintered in microwave are notably finer than those sintered in conventional furnace as a result of much shorter heating time. The mean grain size of conventionally and microwave sintered samples was approximately 6.6 μm and 3.8 μm, respectively. Density and electrical properties of KNN samples sintered at 1115 °C are summarized in Table 2. The bulk density of sample sintered in microwave was 4.22 g/cm^3 (93.8% of theoretical density) which is close to the density of the conventionally sintered sample (4.23 g/cm^3).

As indicated in Table 2, the microwave sintered samples have slightly lower ε_r and higher tan δ compared with conventionally sintered samples. It has been reported in the literature that the dielectric constant is highly dependent on the density of ceramic, which is not the case here because of the similar densities of microwave and conventionally sintered ceramics. The reason can be attributed to the smaller grain size of samples sintered in microwave. According to previous studies [37–40], the grain size has two controversy effects on dielectric properties. On the one hand, the smaller grains may have a higher domain wall density which in turn results in a higher extrinsic contribution on dielectric properties. On the other hand, the smaller grains may exhibit larger internal stresses inside the grains and the absence of 90° domain walls in very fine grains

Table 1
The characteristics of KNN powders calcined at 950 °C in conventional and microwave furnaces.

Calcination method	**Particle Shape**	**Particle size distribution**			**Specific surface area (m^2/g)**	**Powder density (g/cm^3)**	**Phase structure and composition**
		d_{10} (μm)	**d_{50} (μm)**	**d_{90} (μm)**			
Conventional	**Cuboid**	0.5	1.9	4.1	3.7	4.50	Pure orthorhombic KNN
Microwave		0.4	1.2	2.5	4.9	4.50	

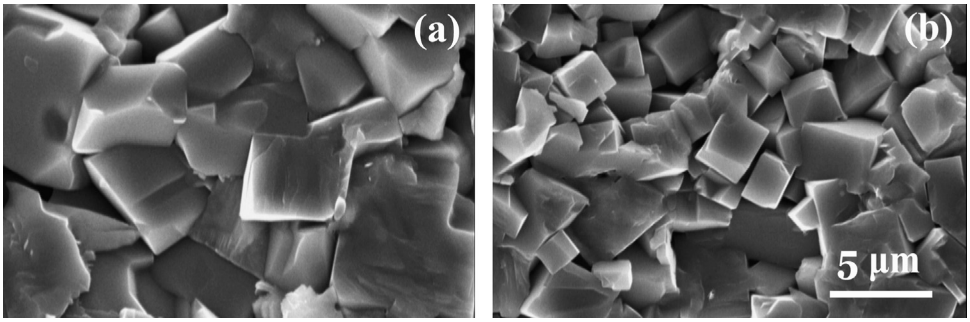

Fig. 6. SEM images of the fracture surface of KNN ceramics sintered in (a) conventional and (b) microwave furnaces at 1115 °C. (Both images have the same magnification, 5000 × .)

Table 2
Summary of physical and electrical properties of conventionally and microwave sintered KNN ceramic at 1115 °C.

Sintering process	**Density (g/cm^3)**	**Relative density (%)**	**Mean grain size (μm)**	**ε_r**	**tan δ**	**d_{33} (pC/N)**	**P_r ($\mu C/cm^2$)**	**E_C (kV/cm)**
Conventional	4.23	94.0	6.6	468	0.031	88	20	12
Microwave	4.22	93.8	3.8	427	0.035	85	18	12

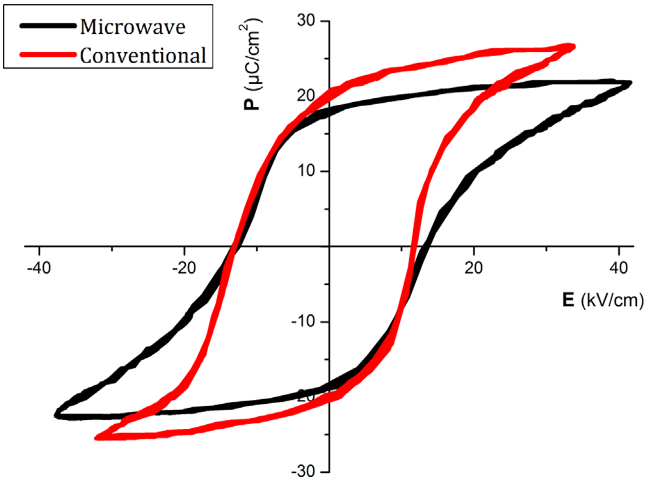

Fig. 7. Polarization versus electric field hysteresis loops for KNN ceramics sintered in conventional and microwave furnaces at 1115 °C.

makes the motion of domain walls difficult and subsequently lower dielectric properties would be expected. In a research by Kumar and Palei [41], they attributed the low dielectric constant of KNN with small grains to the grain boundary width. They also stated that the increase in grain size leads to a decrease in the thickness of more insulating grain boundary layer and eventually, ε_r decreases with decreasing grain size. Moreover, the slightly higher tan δ in microwave sintered samples may be attributed to the difficulty in domain wall motion that results from the smaller grain size [39,42].

The hysteresis loops of polarization versus electric field are shown in Fig. 7. The remnant polarization, P_r, and coercive field, E_C, of sample sintered at 1115 °C in microwave furnace are 18 $\mu C/cm^2$ and 12 kV/cm, respectively. These values are in good agreement with the measured values of conventionally sintered KNN in this work and the values reported by other researchers [14,19]. Although the loops in Fig. 7 have nearly identical values of P_r and E_C, they are different in their slops. The hysteresis loop of microwave sintered sample is tilted compared to the conventionally sintered sample. Tilted loops often appear if there is a surface layer on the top of the samples or surface of the grains [43,44]. This is more likely to happen in ceramics sintered with microwave since they have smaller grains so a surface layer would have a larger effect.

The variations of dielectric constant and loss factor with temperature for samples sintered in conventional and microwave furnaces are shown in Fig. 8. The Curie temperature, T_C, of conventionally and microwave sintered samples are 401 °C and 398 °C, respectively. It is seen that T_C of microwave sintered sample slightly shifted to lower temperatures compared with sample sintered conventionally. Besides, the maximum dielectric constant for conventionally sintered sample is to some extent higher than that sintered in microwave furnace.

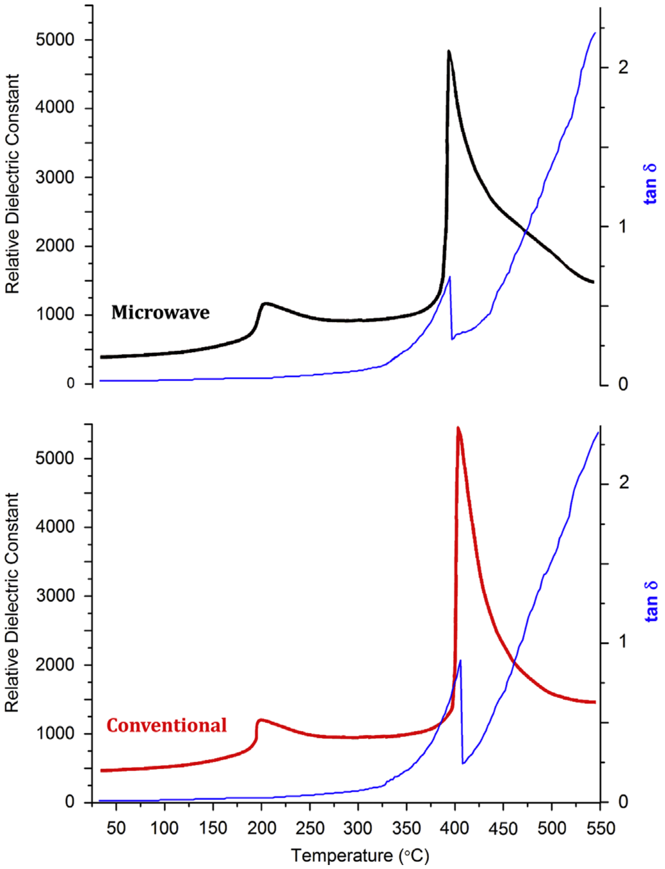

Fig. 8. Temperature dependence of dielectric constant and tan δ for ceramics sintered in conventional and microwave furnaces, measured at 1 kHz.

As Fig. 8 further reveals, the value of tan δ at Curie temperature for sample sintered in conventional furnace is higher than microwave sintered sample, but according to data presented in Table 2, it has a lower value at room temperature. Buixaderas et al. have reported a similar behavior for temperature dependence of dielectric constant and loss for pure KNN with different grain sizes [35].

4. Conclusion

Powder synthesis and sintering of potassium sodium niobate lead-free piezoelectric ceramics were investigated in microwave furnace and compared with conventional synthesis and sintering process. Results showed that by using only about 3% of the total time needed to synthesize the single phase orthorhombic perovskite KNN powder via conventional heating route, powders with close physical characteristics can be obtained by heating in microwave furnace. Moreover, microwave sintering was shown to be a successful method in obtaining dense ceramics with nearly the same dielectric, piezoelectric and ferroelectric behavior as were obtained in conventionally sintered ceramics. Therefore, microwave heating can be regarded as an economical, time-saving and effective method for synthesis and sintering of KNN piezoelectric ceramics.

Acknowledgement

The authors would like to express their sincere gratitude to Prof. D. Damjanovic for his helpful comments and discussions.

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.

[2] W.W. Wolny, European approach to development of new environmentally sustainable electroceramics, Ceramics International 30 (2004) 1079–1083.

[3] E. Ringgaard, T. Wurlitzer, Lead-free piezoceramics based on alkali niobates, Journal of the European Ceramic Society 25 (2005) 2701–2706.

[4] T. Shrout, S. Zhang, Lead-free piezoelectric ceramics: Alternatives for PZT?, Journal of Electroceramics 19 (2007) 111–124.

[5] N. Marandian Hagh, B. Jadidian, A. Safari, Property-processing relationship in lead-free (K,Na,Li)NbO_3-solid solution system, Journal of Electroceramics 18 (2007) 339–346.

[6] F. Rubio-Marcos, J.J. Romero, M.S. Martín-Gonzalez, J.F. Fernández, Effect of stoichiometry and milling processes in the synthesis and the piezoelectric properties of modified KNN nanoparticles by solid state reaction, Journal of the European Ceramic Society 30 (2010) 2763–2771.

[7] J. Hao, Z. Xu, R. Chu, Y. Zhang, Q. Chen, P. Fu, W. Li, G. Li, Q. Yin, Characterization of $(K_{0.5}Na_{0.5})NbO_3$ powders and ceramics prepared by a novel hybrid method of sol–gel and ultrasonic atomization, Materials and Design 31 (2010) 3146–3150.

[8] A. Chowdhury, J. Bould, M.G.S. Londesborough, S.J. Milne, The effect of refluxing on the alkoxide-based sodium potassium niobate sol–gel system: Thermal and spectroscopic studies, Journal of Solid State Chemistry 184 (2011) 317–324.

[9] N. Liu, K. Wang, J.-F. Li, Z. Liu, Hydrothermal synthesis and spark plasma sintering of (K,Na)NbO_3 lead-free piezoceramics, Journal of the American Ceramic Society 92 (2009) 1884–1887.

[10] M. Zhang, M. Guo, Y. Zhou, Low-temperature preparation of $K_xNa_{(1-x)}$ NbO_3 lead-free piezoelectric powders by microwave-hydrothermal synthesis, International Journal of Applied Ceramic Technology 8 (2011) 591–596.

[11] T. Rojac, A. Benčan, H. Uršič, B. Malič, M. Kosec, Synthesis of a Li- and Ta-modified (K,Na)NbO_3 solid solution by mechanochemical activation, Journal of the American Ceramic Society 91 (2008) 3789–3791.

[12] J. Zhu, Z. Li, Z. Xu, X. Yao, Mechanochemical synthesis of $K_xNa_{1-x}NbO_3$ powders, Ferroelectrics 401 (2010) 211–217.

[13] H. Du, Z. Li, F. Tang, S. Qu, Z. Pei, W. Zhou, Preparation and piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$ lead-free piezoelectric ceramics with pressure-less sintering, Materials Science and Engineering: B 131 (2006) 83–87.

[14] B.-P. Zhang, L.-M. Zhang, J.-F. Li, X.-N. Ding, H.-L. Zhang, Effect of sintering temperature on electrical properties of $Na_{0.5}K_{0.5}NbO_3$ lead-free piezoelectric ceramics prepared by normal sintering, Ferroelectrics 358 (2007) 188–195.

[15] R.E. Jaeger, L. Egerton, Hot pressing of potassium-sodium niobates, Journal of the American Ceramic Society 45 (1962) 209–213.

[16] G.H. Haertling, Properties of hot-pressed ferroelectric alkali niobate ceramics, Journal of the American Ceramic Society 50 (1967) 329–330.

[17] R. Wang, R. Xie, T. Sekiya, Y. Shimojo, Fabrication and characterization of potassium–sodium niobate piezoelectric ceramics by spark-plasma-sintering method, Materials Research Bulletin 39 (2004) 1709–1715.

[18] J.-F. Li, K. Wang, B.-P. Zhang, L.-M. Zhang, Ferroelectric and piezoelectric properties of fine-grained $Na_{0.5}K_{0.5}NbO_3$ lead-free piezoelectric ceramics prepared by spark plasma sintering, Journal of the American Ceramic Society 89 (2006) 706–709.

[19] R. Zuo, J. Rodel, R. Chen, L. Li, Sintering and electrical properties of lead-free $Na_{0.5}K_{0.5}NbO_3$ piezoelectric ceramics, Journal of the American Ceramic Society 89 (2006) 2010–2015.

[20] R. Hayati, M. Feizpour, A. Barzegar, Effect of nano ZnO additive on the microstructure and electrical properties of potassium-sodium niobate

lead-free piezoelectric ceramics, in: Proceedings of the 2009 9th IEEE Conference on Nanotechnology, IEEE-NANO 2009, pp. 273–276.

[21] M. Oghbaei, O. Mirzaee, Microwave versus conventional sintering: A review of fundamentals, advantages and applications, Journal of Alloys and Compounds 494 (2010) 175–189.

[22] V.K. Saxena, U. Chandra, Microwave Synthesis: A Physical Concept, in: U. Chandra (Ed.), Microwave Heating, InTech, 2011.

[23] K.H. Brosnan, G.L. Messing, D.K. Agrawal, Microwave sintering of alumina at 2.45 GHz, Journal of the American Ceramic Society 86 (2003) 1307–1312.

[24] T. Ebadzadeh, M.H. Sarrafi, E. Salahi, Microwave-assisted synthesis and sintering of mullite, Ceramics International 35 (2009) 3175–3179.

[25] S. Swain, P. Kumar, D.K. Agrawal, Sonia, Dielectric and ferroelectric study of KNN modified NBT ceramics synthesized by microwave processing technique, Ceramics International 39 (2013) 3205–3210.

[26] P.Y. Chen, C.S. Chen, C.C. Chou, T.Y. Tseng, H.D. Chen, Microstructures and electrical properties of lead-based PBZNZT and lead-free BNKT piezoelectric ceramics using microwave sintering, Current Applied Physics 11 (2011) S110–S119.

[27] H. Nagata, K. Matsumoto, T. Hirosue, Y. Hiruma, T. Takenaka, Fabrication and electrical properties of potassium niobate ferroelectric ceramics, Japanese Journal of Applied Physics 46 (2007) 7084–7088.

[28] M. Feizpour, Study and Developement of Lead-free Piezoelectric Ceramics Based on Alkali Niobates, in: Materials Science and Engineering–Electroceramics, M.Sc. Thesis, Shiraz University, Shiraz, Iran (Islamic Republic of), 2009, pp. 158.

[29] R.A. Nyquist, R.O. Kagel, Infrared Spectra of Inorganic Compounds, Academic Press, New York & London, 1971.

[30] M.d.C.B. López, G. Fourlaris, B. Rand, F.L. Riley, Characterization of barium titanate powders: Barium carbonate identification, Journal of the American Ceramic Society 82 (1999) 1777–1786.

[31] C. Wang, Y. Hou, H. Ge, M. Zhu, H. Wang, H. Yan, Sol–gel synthesis and characterization of lead-free LNKN nanocrystalline powder, Journal of Crystal Growth 310 (2008) 4635–4639.

[32] N. Kumada, T. Kyoda, Y. Yonesaki, T. Takei, N. Kinomura, Preparation of $KNbO_3$ by hydrothermal reaction, Materials Research Bulletin 42 (2007) 1856–1862.

[33] Y. Chang, Z. Yang, X. Chao, R. Zhang, X. Li, Dielectric and piezoelectric properties of alkaline-earth titanate doped $(K_{0.5}Na_{0.5})NbO_3$ ceramics, Materials Letters 61 (2007) 785–789.

[34] L. Egerton, D.M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate, Journal of the American Ceramic Society 42 (1959) 438–442.

[35] E. Buixaderas, V. Bovtun, M. Kempa, M. Savinov, D. Nuzhnyy, F. Kadlec, P. Vanek, J. Petzelt, M. Eriksson, Z. Shen, Broadband dielectric response and grain-size effect in $K_{0.5}Na_{0.5}NbO_3$ ceramics, Journal of Applied Physics 107 (2010) 014111.

[36] E. Hollenstein, Dielectric and Piezoelectric Properties of Potassium Sodium Niobate Ceramics, in: Ceramics Laboratory, Ph.D. Dissertation, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland, 2007, pp. 143.

[37] G. Arlt, D. Hennings, G. de With, Dielectric properties of fine-grained barium titanate ceramics, Journal of Applied Physics 58 (1985) 1619–1625.

[38] W. Cao, C.A. Randall, Grain size and domain size relations in bulk ceramic ferroelectric materials, Journal of Physics and Chemistry of Solids 57 (1996) 1499–1505.

[39] C.A. Randall, N. Kim, J.-P. Kucera, W. Cao, T.R. Shrout, Intrinsic and extrinsic size effects in fine-grained morphotropic-phase-boundary lead zirconate titanate ceramics, Journal of the American Ceramic Society 81 (1998) 677–688.

[40] J. Hao, W. Bai, W. Li, J. Zhai, Correlation between the microstructure and electrical properties in high-performance $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ lead-free piezoelectric ceramics, Journal of the American Ceramic Society 95 (2012) 1998–2006.

[41] P. Kumar, P. Palei, Effect of sintering temperature on ferroelectric properties of $0.94(K_{0.5}Na_{0.5})NbO_3$–0.06 $LiNbO_3$ system, Ceramics International 36 (2010) 1725–1729.

[42] S. Huo, S. Yuan, Z. Tian, C. Wang, Y. Qiu, Grain size effects on the ferroelectric and piezoelectric properties of $Na_{0.5}K_{0.5}NbO_3$ ceramics prepared by Pechini method, Journal of the American Ceramic Society 95 (2012) 1383–1387.

[43] D. Damjanovic, Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics, Reports on Progress in Physics 61 (1998) 1267–1324.

[44] D. Damjanovic, Hysteresis in Piezoelectric and Ferroelectric Materials, in: G. Bertotti, I. Mayergoyz (Eds.), Science of Hysteresis, vol. III, Academic Press, 2006, pp. 337–465.