

Effect of High-Energy Ball Milling on the Electrical and Piezoelectric Properties of $(K_{0.5}Na_{0.5})(Nb_{0.9}Ta_{0.1})O_3$ Lead-Free Piezoceramics

Chongtham Jiten, K. Chandramani Singh, Radhapiyari Laishram

Abstract—Nanocrystalline powders of the lead-free piezoelectric material, tantalum-substituted potassium sodium niobate $(K_{0.5}Na_{0.5})(Nb_{0.9}Ta_{0.1})O_3$ (KNNT), were produced using a Retsch PM100 planetary ball mill by setting the milling time to 15h, 20h, 25h, 30h, 35h and 40h, at a fixed speed of 250rpm. The average particle size of the milled powders was found to decrease from 12nm to 3nm as the milling time increases from 15h to 25h, which is in agreement with the existing theoretical model. An anomalous increase to 98nm and then a drop to 3nm in the particle size were observed as the milling time further increases to 30h and 40h respectively. Various sizes of these starting KNNT powders were used to investigate the effect of milling time on the microstructure, dielectric properties, phase transitions and piezoelectric properties of the resulting KNNT ceramics. The particle size of starting KNNT was somewhat proportional to the grain size. As the milling time increases from 15h to 25h, the resulting ceramics exhibit enhancement in the values of relative density from 94.8% to 95.8%, room temperature dielectric constant (ϵ_{RT}) from 878 to 1213, and piezoelectric charge coefficient (d_{33}) from 108pC/N to 128pC/N. For this range of ceramic samples, grain size refinement suppresses the maximum dielectric constant (ϵ_{max}), shifts the Curie temperature (T_C) to a lower temperature and the orthorhombic-tetragonal phase transition (T_{ot}) to a higher temperature. Further increase of milling time from 25h to 40h produces a gradual degradation in the values of relative density, ϵ_{RT} , and d_{33} of the resulting ceramics.

Keywords—Ceramics, Dielectric, High-energy milling, Perovskite.

I. INTRODUCTION

RESEARCH on lead-free piezoelectric ceramics [1],[2] has been gaining importance due to the environmental concern caused by highly toxic nature of lead-based ceramics. For finding a replacement, attempts have been being made towards developing several lead-free piezoelectric materials such as Bi-based perovskite [3], Bi-layered materials [4], tungsten-bronze-type materials [5], $BaTiO_3$ -based materials [6], and alkaline niobate-based materials [7]-[10]. Among the alkaline niobate-based perovskite-type ceramics, the composition $(K_{0.5}Na_{0.5})NbO_3$, a solid solution of ferroelectric

$KNbO_3$ and antiferroelectric $NaNbO_3$, is considered one of the most promising candidates because of its excellent piezoelectric properties, high Curie temperature (T_C) of over 400°C and low anisotropy [1], [2]. However, it is very difficult to obtain dense and well-sintered KNN ceramics by conventional sintering technique due to high volatility of potassium element at high temperatures and instability of the crystal phase [2]. An important aspect for improving the sinterability of KNN ceramics is the reduction in initial particle size, due to the fact that the driving force for sintering is inversely proportional to the particle size [11]. There are reports of great improvement on the physical, electrical and piezoelectric properties of lead free $BaTiO_3$ (BT) ceramics synthesized from the nanocrystalline powders [12]-[14]. It is reported that the dielectric constant is strongly dependent on the particle size [15]. In ferroelectrics, it is reported that ferroelectricity decreases with decreasing particle size and disappears below certain critical size [16], [17]. It is believed that below the critical size the lattice changes from tetragonal to cubic and ferroelectricity is lost. For BT the possible average critical particle size for ferroelectric behavior in dense BT nanocrystalline ceramics is below 50nm [18]. These results highlight the importance of the production of nanocrystalline powders having desired particle size. There are varieties of routes for the synthesis of nanoceramic powders such as chemical coprecipitations [19], sol-gel technique [20], hydrothermal synthesis [21]. However, the high-energy ball milling technique is still considered as a simple and cost effective method for large scale production of nanoceramic powders [12], [22], [23]. It is found that high-energy milling is an effective way to modify the morphology, reduce the particle size and thus enhance the densification behavior of ferroelectric powders. We present results on the production of KNNT nanopowders by planetary ball milling under different milling conditions, and the electrical and piezoelectric properties of the corresponding ceramics.

II. EXPERIMENTAL

The starting materials were AR grade powders of K_2CO_3 , Na_2CO_3 , Ta_2O_5 and Nb_2O_5 (Aldrich, purity $\geq 99\%$). The powders were weighed in proportion to the stoichiometric ratio to yield $(K_{0.5}Na_{0.5})(Nb_{0.9}Ta_{0.1})O_3$ and homogeneously mixed in isopropanol medium using ball milling in plastic bottle with zirconia balls. The mixture was dried and calcined at 900°C for 4h. In order to enhance the compositional uniformity, the powder was calcined twice under the same

Chongtham Jiten is with the Department of Physics, Kirori Mal College, University of Delhi, New Delhi 110007, Delhi, India (e-mail: jitenchong@gmail.com.)

K. Chandramani Singh is with the Department of Physics, Sri Venkateswara College, University of Delhi, New Delhi-110021, India (Corresponding Author, Phone: 91-11-27457625, e-mail: kongbam@gmail.com)

Radhapiyari Laishram is with the Solid State Physics Laboratory, Lucknow Road, Timarpur, Delhi – 110054, India (e-mail: l_radhapiyari@hotmail.com)

conditions. The calcined powder was high-energy milled in isopropanol medium using a Retsch PM 100 planetary ball mill in which the sun wheel and grinding jar rotate in opposite directions with speed ratio of 1:-2. Agate vial and balls were used. The milling was performed for 15, 20, 25, 30, 35 and 40h, fixing the speed at 250rpm. During each milling, a mass ratio of 1:5 for powder and balls was always maintained. The powder charge taken for milling was about 10g. The ball mill was set to a rotational mode that reverses the rotational direction of the vial and the sun wheel every 6 minutes after a rest interval of 2 minutes to cool down the milling system.

The particle sizes of the powders were examined by using TEM (Morgagni 268). After drying, the milled powders were granulated by adding 5-wt% poly vinyl alcohol as a binder and were uniaxially pressed into circular pellets of 10mm diameter and 1mm thickness at 200MPa. After burning off the binder, the pellets were sintered in a covered alumina crucible at 1050°C for 1h in air. The sintered pellets (to be abbreviated as KNNT15, KNNT20, KNNT25, KNNT30, KNNT35, and KNNT40 respectively) were lapped to a thickness of 0.6mm.

The bulk density of the sintered compacts was obtained by Archimedes method. X-ray Diffractometer (Philips Diffractometer PW 3020) with monochromatic CuK_α radiation ($\lambda=1.54178\text{\AA}$) was used over a 2θ angle from 20° to 70° to determine the crystal structures of the sintered specimens. The microstructures of the fractured surfaces of the samples were studied using SEM (Leo 1430, Japan).

For electrical measurements, silver paste was applied on both sides of the sintered samples as electrodes and fired at 200°C for 1h. The temperature dependence of dielectric properties was measured with an impedance analyzer (Wayne Kerr 6505B). For activating piezoelectric properties to the ceramics, the samples were immersed in silicone oil and poled under a DC field of 3kV/mm at 100°C for 30min, and then the samples were cooled to room temperature by maintaining the electric field. The piezoelectric charge coefficient (d_{33}) was measured with a Piezometer (Take Control, PM 25).

III. RESULTS AND DISCUSSION

The average particle sizes of the KNNT powders milled at 250 rpm for 15h, 20h, 25h, 30h, 35h and 40h were found to be 12nm, 7nm, 3nm, 98nm, 12nm and 3nm respectively. Fig. 1 shows the XRD patterns for the KNNT ceramics prepared from these powders. All the ceramics exhibit single phase perovskite structure. No trace of any secondary phase was detected.

All the samples of KNNT ceramics showed no deliquescence when they were exposed to water for 24h. The dependence of density of the ceramics on the milling time of the starting powders is shown in Fig. 2. All samples reached a bulk density of $> 92\%$ of the theoretical density, a reasonably high value for such ceramics. The reduction in the particle size to the nanoscale by high energy milling has promoted the otherwise difficult densification of the ceramic system, as the driving force for sintering is inversely proportional to the initial particle size [24].

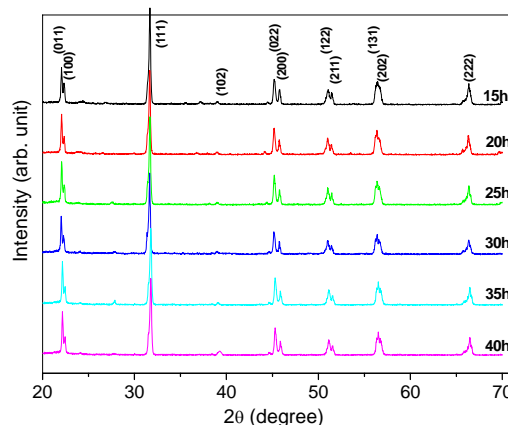


Fig. 1 XRD patterns of KNNT ceramics prepared from various milled powders

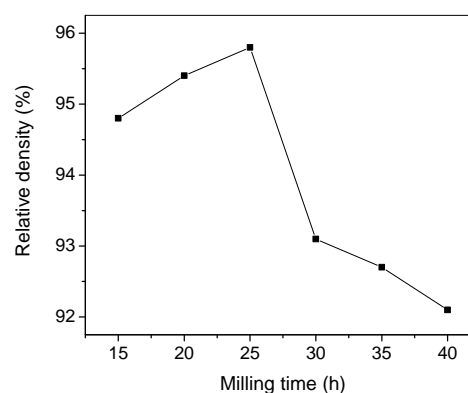


Fig. 2 Relative density of KNNT ceramics

Fig. 3 shows the SEM micrographs of the fractured surfaces of the ceramics. A quasi-cubic morphology is apparent for all the samples, which is one of the reasons for poor sinterability of KNN ceramics. The grain sizes become finer and their distribution becomes more homogeneous with fewer pores as the initial particle sizes decrease to 3nm at 25-h milling. Thus the enhanced densification of KNNT ceramics in the range 15h-25h (Fig. 2) as a result of high-energy ball milling is readily attributed to the refined particles/grains. This is because refined particles/grains are more reactive. A less regular morphology with more porosity is seen in the sample prepared from 98-nm powders (Fig. 3 (d)). Though the grain size follows a decreasing trend as we move from KNNT25 to KNNT40, grains are seen to be much less densely packed in these samples (Figs. 3 (d)-(f)). The observation is in agreement with the density variation of the samples. It can be noted that there are marked differences between the microstructures of KNNT15 and KNNT35, despite both being prepared from 12-nm powders, and those of KNNT25 and KNNT40, prepared from 3-nm powders.

Fig. 4 shows the temperature dependence of dielectric constant (ϵ') for KNNT ceramics, measured at 100kHz. All the ceramics exhibit two transition peaks: one is associated with the cubic-tetragonal phase transition at T_c and the other is the

tetragonal–orthorhombic phase transition at T_{ot} .

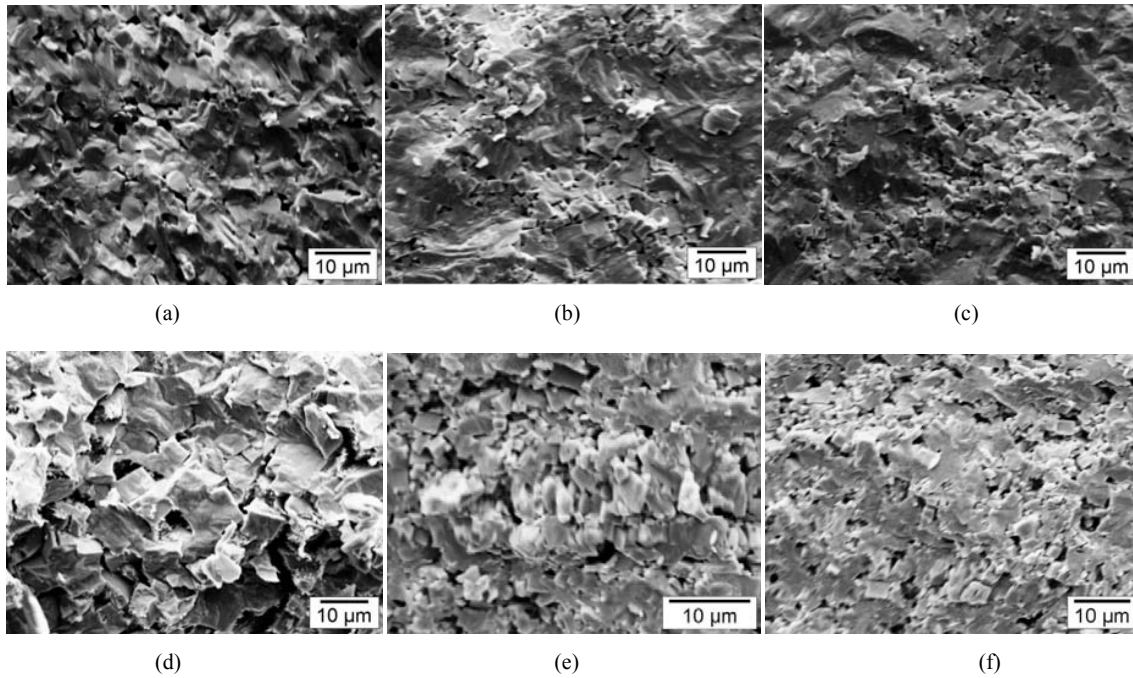


Fig. 3 SEM micrographs of KNNT ceramics milled at 250rpm for (a) 15h, (b) 20h, (c) 25h, (d) 30h, (e) 35h, and (f) 40h.

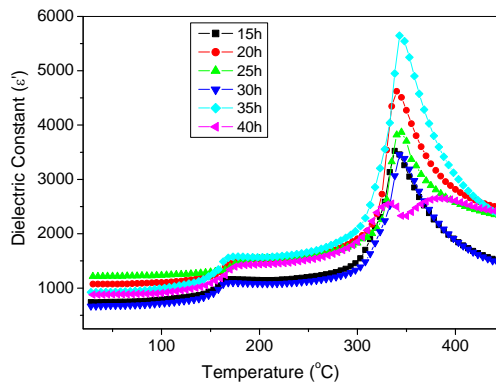


Fig. 4 Temperature dependence of dielectric constant, measured at 100kHz, for KNNT ceramics.

Figs. 5 (a), (b) show the dependence of T_{ot} , T_c , ϵ_{RT} and ϵ_{max} for KNNT ceramics on milling time of the starting powders. As seen in this figure, with increasing milling time from 15h to 25h, T_c decreases, T_{ot} increases, ϵ_{RT} increases and ϵ_{max} decreases. These results are in agreement with those observed for BaTiO₃ ceramic system in which grain size refinement not only caused T_c to decrease and T_{ot} to increase, but also enhanced the base line intensity at lower temperatures and reduced the intensity at high temperatures, which was responsible for internal stress in small-grained ceramic [25]-[27]. The increase in ϵ_{RT} from KNNT15 to KNNT25 can be attributed to the denser microstructure and decreasing grain size. The higher value ϵ_{RT} for fine-grain microstructures result from a contribution from residual stresses on individual grains,

where the grains become substantially untwined with decreasing grain size [24]. The decreasing trend of ϵ_{RT} after KNNT25 results from the corresponding fall in density due to porous microstructure. The presence of porosity decreases the dielectric constant of materials because the relative dielectric constant of pores/vacuum is unity.

The dependence of piezoelectric charge constant (d_{33}) of the KNNT ceramic samples on milling time are shown in Fig. 6. The piezoelectric charge constant (d_{33}) varied in the range of 67-128pC/N. The d_{33} value of 128 pC/N for the ceramic prepared from 3-nm powders corresponding to the milling time of 25h is appreciably high as compared with those published for pure KNN samples sintered under atmospheric conditions [24], [28], [29]. The increase in d_{33} can be attributed to the denser microstructure. Even if the particle size reduces to 3-nm level again at 40-h milling, the resulting ceramic exhibits poorer dielectric and piezoelectric properties. This is attributed to the lower density associated the more porous microstructure of the ceramic consequent upon prolonged milling of the starting powders.

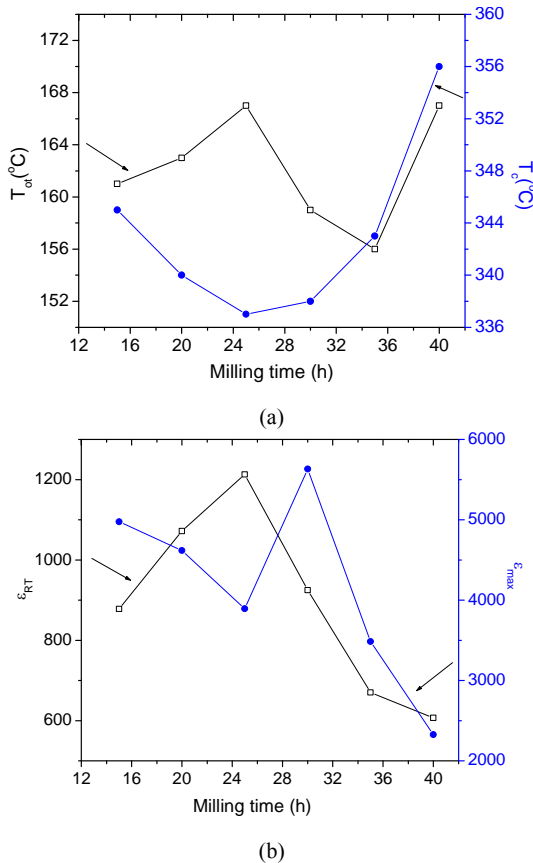


Fig. 5 Dependence of (a) T_{0r} and T_c , (b) ϵ_{RT} and ϵ_{max} , on milling time, for KNNT ceramics

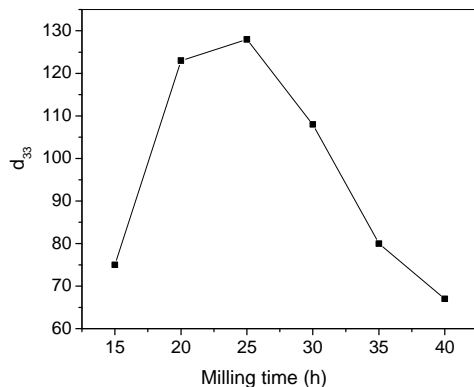


Fig. 6 Dependence of d_{33} on milling time for KNNT ceramics

IV. CONCLUSION

Lead-free KNNT nanocrystalline powders with various particle sizes have been produced by high-energy ball milling. An increase in milling time from 15h to 25h at a fixed speed of 250rpm yields powders with average particle size decreasing from 12nm to a minimum of about 3nm. The particle size then increases to 98nm as the milling time increases to 30h, before it finally decreases to 3nm at 40-h milling. The ceramic prepared from 3-nm powders

corresponding to 25-h milling possesses the optimum dielectric constant of 1213 and piezoelectric coefficient of 128pC/N. The ceramic prepared from 3-nm powders corresponding to 40-h milling shows deterioration in the dielectric and piezoelectric properties, which has been attributed to a porous microstructure resulting from prolonged milling of the starting powders.

ACKNOWLEDGMENT

The authors acknowledge the financial support from the Department of Science and Technology, India, under the Research Project No. SR/S2/CMP-0017/2011.

REFERENCES

- [1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya and M. Nakamura: Nature Vol. 432 (4) (2004), p. 84.
- [2] M. D. Maeder, D. Damjanovic and N. Setter: J. Electroceram. Vol. 13 (2004), p. 385.
- [3] H. Nagata, M. Yoshida, Y. Makiuchi and T. Takenaka: Jpn. J. Appl. Phys. Vol. 42 (2003) p. 7401.
- [4] M. Suzuki, H. Nagata, J. Ohara, H. Funakubo and T. Takenaka: Jpn. J. Appl. Phys. Vol. 42 (2003), p. 6090.
- [5] R. J. Xie, Y. Akimune, R. Wang, N. Hirotsaki, and T. Nishimura: Jpn. J. Appl. Phys. Vol. 42 (2003), p. 7404.
- [6] Z. Yu, C. Ang, R. Guo and A. S. Bhalla: Jpn. J. Appl. Phys. Vol. 92 (2002), p. 1489.
- [7] R. E. Jaeger and L. Egerton: J. Am. Ceram. Soc. Vol. 45 (1962), p. 208.
- [8] R. Wang, R. Xie, T. Sekiya, Y. Shimojo, Y. Akimune, N. Hirotsaki and M. Itoh: Jpn. J. Appl. Phys. Vol. 41 (2002), p. 7119.
- [9] R. Wang, R. Xie, T. Sekiya and Y. Shimojo: Mater. Res. Bull. Vol. 39 (2004), p. 1709.
- [10] M. Matsubara, T. Yamaguchi, K. Kikuta and S. Hirano: Jpn. J. Appl. Phys. Vol. 44 (2005), p. 258.
- [11] R. Zuo, J. Rodel, R. Chen and L. Li: J. Am. Ceram. Soc. Vol. 89(6) (2006), p. 2010.
- [12] L. B. Kong, T. S. Zhang, J. Ma and F. Boey: Prog. Mater. Sci. Vol. 53 (2008), p. 207.
- [13] T. Karaki, K. Yan, T. Miyamoto and M. Adachi: Jpn. J. Appl. Phys. Vol. 46 (2007), p. L97.
- [14] H. Takahashi, Y. Numamoto, J. Taaani, K. Maatsuta, J. Qiu and S. Tsurekawa: Jpn. J. Appl. Phys. Vol. 45 (2006), p. L30.
- [15] K. Wu and W. Schlitz: J. Am. Cer. Soc. Vol. 75 (1992), p. 3390.
- [16] K. Ishikawa, K. Yoshikawa and N. Okada: Phys. Rev. B Vol. 37 (1988), p. 5852.
- [17] M. H. Frey and D. A. Payne: Phys. Rev. B Vol. 54 (1996), p. 3158.
- [18] Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu, A. Testino, M. Nygren, M. Johnsson and P. Nanni: Phys. Rev. B Vol. 70 (2004), p. 024107.
- [19] M. Buscaglia, Z. Zhao, V. Buscaglia, M. Viviani, M. T. Buscaglia, L. Mitoseriu and Testino: Nanotech. Vol. 15 (2004), p. 1113.
- [20] J. Cho and M. Kubawara: J. Eur. Ceram. Soc. Vol. 24 (2004), p. 2959.
- [21] H. Xu, L. Gao and J. Guo: J. Eur. Ceram. Soc. Vol. 22 (2002), p. 1163.
- [22] T. Venugopal, K. P. Rao and B. S. Murty: J. Nanosci. Nanotechnol. Vol. 7 (2007), p. 2376.
- [23] Y. Wang, Y. Li, C. Rong and P. Liu: J. Nanotechnol. Vol. 18 (2007), p. 465701.
- [24] Zuo R, Rodel J, Chen R, Li L. J Am Ceram Soc 2006; 89(6): 2010-15
- [25] A. Yamaji, Y. Enomoto, K. Kinoshita and T. Murakami, J. Am. Ceram. Soc. Vol. 64 (1977), p. 97.
- [26] K. Kinoshita and A. Yamaji, J. Appl. Phys. Vol. 47 (1976), p. 371.
- [27] W.R. Buessem, L.E. Cross and A.K. Goswami: J. Am. Ceram. Soc. Vol. 49 (1966), p. 33.
- [28] Guo Y, Kakimoto K, Ohsato H. Appl Phys Lett 2004; 85(18): 4121-3.
- [29] Jaeger RE, Egerton L. J Am Ceram Soc 1962; 45(5): 209-13.