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Short communication

Effect of oxygen sintering on the structural and electrical properties of KNN ceramics

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Abstract

Single perovskite phase of $K_{0.5}Na_{0.5}NbO_3$ (KNN) system was obtained at low calcination temperature (450 °C) by combustion method using urea as fuel. The sintering of the KNN sample was performed at 1120 °C for 2 h in the oxygen rich environment. SEM micrograph showed the dense and non-uniform distribution of grains with grain size ~1.45 μm. The experimental density of the oxygen sintered KNN samples was found to be ~4.398 g/cc, which is higher than the same system sintered in air by mixed oxide method.

Keywords: A. Sintering; Ceramics; Ferroelectrics

1. Introduction

The lead zirconate titanate (PZT) based materials with compositions close to the morphotropic phase boundary (MPB) have been widely used for piezoelectric actuators, sensors and transducers applications [1–3]. However, the high toxicity of lead oxide has caused serious environmental problems. Therefore, nowadays extensive research is going on to find suitable lead-free systems with potentially good piezoelectric and ferroelectric properties [4]. Recently, $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based systems have attracted much attention because of having high piezoelectric properties, high Curie temperature (T_c) and environmental friendly nature [5–11]. A major problem concerning KNN system is to obtain high density samples by using conventional solid state reaction route (CSSR). It was also reported that KNN based ceramics were sensitive to moisture and only hot-pressed samples could be sufficiently densified [12]. Recently developed spark plasma sintering technique is another method to produce dense bulk samples of KNN ceramics with relatively better density [13]. Although these methods can yield high densities and better piezoelectric properties compared to KNN ceramics synthesized by CSSR, but still it is obvious that normal or pressureless sintering of these materials is more suitable for mass production. It is well known that with the use of ultrafine powders the densification of a ceramic can be enhanced. Hence, recently some researchers have tried to synthesize ultra fine powders by wet chemical methods. Among the wet chemical methods, sol–gel method is usually employed to prepare KNN powders in which alkoxides of niobium are generally used as Nb sources. However, certain inherent problems are associated with Nb alkoxides, such as inammability, relatively high cost, and great sensitivity to moisture [14]. It has been reported that combustion synthesis is an attractive technique for the synthesis of different materials, such as $BaTiO_3$, which involves a self-sustained reaction between reactive materials and fuel (e.g. urea), and the reaction converts the initial mixture typically to fine well crystalline powders of desired compositions [15]. Hence, in order to obtain ultrafine KNN powder combustion technique, which is a fast, energy-efficient and environmental friendly chemical process has been used [16]. It was also reported that sintering of the KNN based ceramics in the oxygen rich environment can be very effective to obtain high experimental density and better ferroelectric properties [17]. In the present work the KNN ceramics have been synthesized by combustion technique at lower calcination temperature. The effect of oxygen environment sintering on the microstructral and electrical properties has been studied and discussed in detail.

2. Experimental procedure

Lead free KNN samples were synthesized by combustion synthesis method using urea as a fuel. Sodium carbonate

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(Na_2CO_3, 99.9% purity), potassium carbonate (K_2CO_3, 99.9% purity), niobium pentoxide (Nb_2O_5, 99.9% purity) and urea were used as starting materials. Stoichiometric weights of Na_2CO_3, K_2CO_3 and Nb_2O_5 powders were mixed and ball milled with acetone for 8 h, using zirconia balls as the grinding media. The obtained oxide powder was mixed with urea with a weight ratio varying from 1:0.75 to 1:1.25 (KNN:Urea) by wet ball-milling for 2 h. After drying the obtained slurry in an oven, the calcination was carried out at four different temperatures ranging from 350 °C to 500 °C for 6 h, respectively. The calcined powder was mixed thoroughly with 2 wt% polyvinyl alcohol (PVA) binder and pressed into disks of diameter ~10 mm and a thickness of ~1.5 mm under a pressure ~60 Mpa. The sintering of the samples was carried out at 1120 °C for 2 h in oxygen rich environment with a heating rate of 5 °C/min. XRD analysis of the sintered KNN samples was performed on a PW 3020 Philips diffractometer using Cu Kα ($\lambda = 0.15405$ nm) radiation. The sintered microstructures were observed using a JEOL T-330 scanning electron microscope (SEM). The experimental densities (d_{ex}) of the samples were measured by the Archimedes method. Silver paste was applied on both sides of the samples for the electrical measurements. Dielectric constant (ε_r) and dielectric loss ($\tan\delta$) were measured as a function of temperature using a computer interfaced HIOKI 3532-50 LCR-HITESTER. A conventional Sawyer–Tower circuit was used to measure the electric field vs polarization hysteresis (*P*–*E*) loop at 20 Hz frequency. The samples for the piezoelectric property measurements were poled at 150 °C by applying a dc electric field of 3 kV/mm for 30 min by corona poling. The d_{33} value of the sample was measured by Piezo meter.

3. Results and discussions

The XRD patterns of urea mixed KNN samples calcined at 450 °C for 6 h with different weight ratios (1:0.75–1:1.25) are shown in Fig. 1. Single perovskite phase developed in case of 1:1 weight ratio of KNN powder and urea, whereas in other ratios secondary phases are detected. This may be due to the fact that the uniformity of oxide mixture varies with the variation of urea ratio [16]. Fig. 1(b) shows the XRD patterns of urea mixed KNN powders (1:1) calcined at different temperatures starting from 350 °C to 500 °C for 6 h, respectively. As shown in Fig. 1(b), the phase purity and crystallinity of the urea mixed KNN (1:1) samples is found to increase with the increase in calcinations temperature. At lower calcinations temperature, secondary phase peaks are detected, but single perovskite phase has been confirmed at 450 °C. Whereas, in the same system synthesized by solid state reaction route single perovkite phase developed at ~850 °C [18]. This shows the importance of using urea as a fuel for the low temperature synthesis of KNN powder. The basic principle of reduction of processing temperature by using fuel is that when an organic compound combusts within a mixture, it gives out heat that can be effectively supplied to the raw powders in the mixture. The energy supplied in this way accelerates the chemical reaction between raw powders and also reduces the reaction temperature.

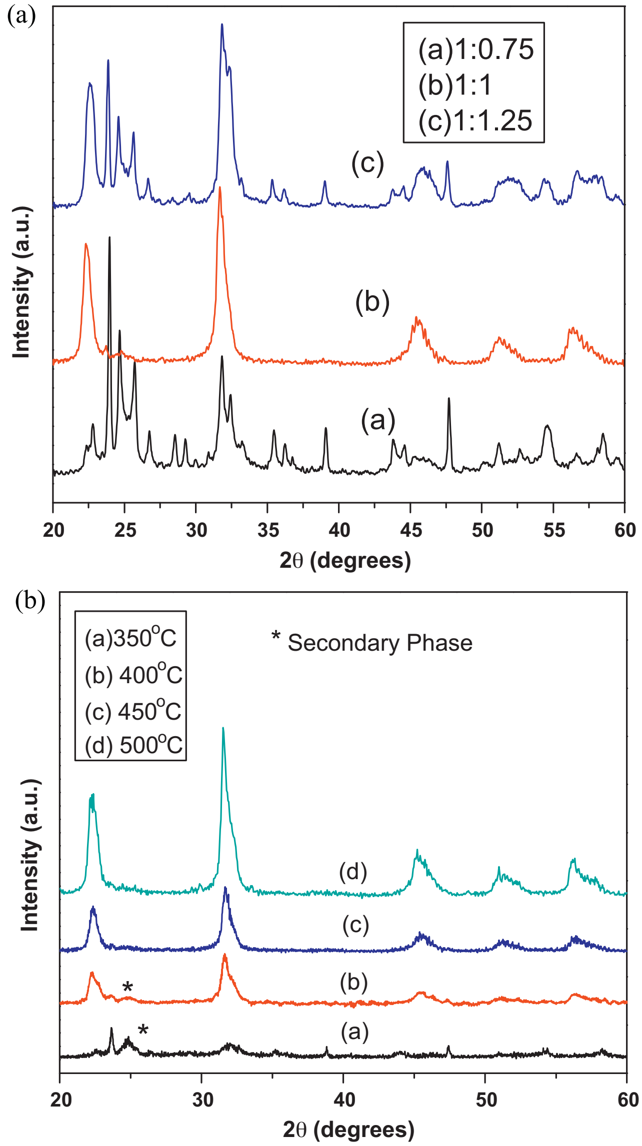

Fig. 1. (a) XRD patterns of urea mixed KNN powders calcined at 450 °C and (b) XRD patterns of 1:1 weight ratio of KNN powder and urea calcined at different temperatures.

Fig. 2 shows the XRD patterns of the 1:1 urea mixed KNN sample sintered at 1120 °C for 2 h in the oxygen rich environment. The diffraction lines are indexed in different crystal systems and unit cell configurations using a computer program package 'Powdmult'. Standard deviations, S.D, $\sum\Delta d = (d_{obs} - d_{cal})$, where '*d*' is inter-plane spacing, is found to be minimum for orthorhombic structure. The lattice parameters and unit cell volume are found to be $a = 3.9435$ Å, $b = 4.0019$ Å, $c = 4.0122$ Å and $V = 63.32$ Å^3 whereas the X-ray density (d_x) of the sample was found to be ~4.508 g/cc. The (d_x) of the sample was calculated by using the formula; $d_x = ((\Sigma A/N)/V)n$; where d_x is the X-ray density, ΣA is the sum of the atomic weights of all the atoms in the unit cell, N is the Avogadro's number, V is the volume of the unit cell and n is the number of atoms per unit cell of the crystal structure.

Fig. 3 shows the SEM micrograph of the KNN sample sintered at 1120 °C for 2 h in the oxygen rich environment.

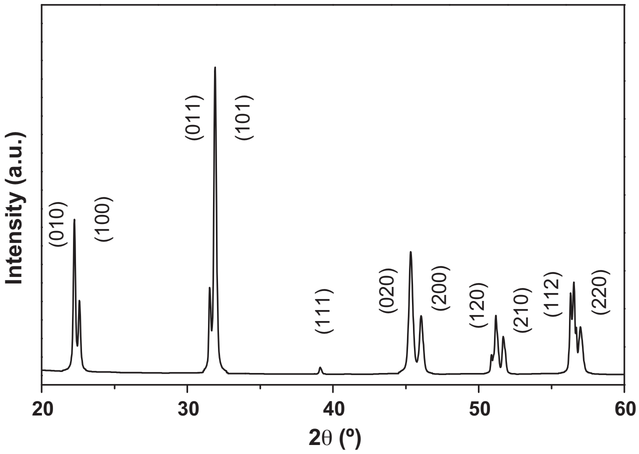

Fig. 2. XRD patterns of 1:1 urea mixed KNN samples sintered at 1120 °C/2 h.

Surface morphology shows the rectangular size grains with dense packing. The average grain size of the oxygen sintered KNN sample is calculated by linear intercept method and is found to be ~1.45 μm. The experimental density (d_{ex}) of the sample is found to be ~4.398 g/cc which is ~97.6% of the d_x. It is also seen that the oxygen sintered KNN sample is denser than the same system sintered in air by the conventional solid-state method [19].

Fig. 4 shows the temperature dependence of the dielectric constant (ε_r) at different frequencies of oxygen sintered KNN sample. The room temperature (RT) ε_r value of KNN sample at 1 kHz frequency is found to be ~490. Two phase transitions are clearly observed in the dielectric permittivity vs. temp curve corresponding to the phase transitions from orthorhombic to tetragonal (~220 °C) and tetragonal to cubic (~420 °C), respectively. The phase transition occurred ~220 °C is the ferroelectric phase transition temperature whereas the transition ~420 °C is called as the ferroelectric–paraelectric phase transition temperature (Curie temperature).

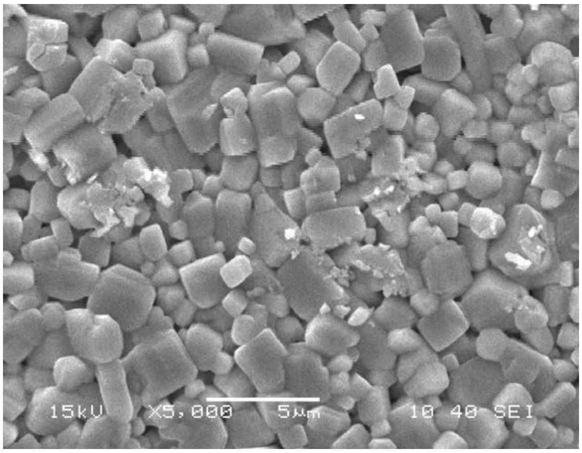

Fig. 3. SEM micrograph of KNN samples sintered at 1120 °C.

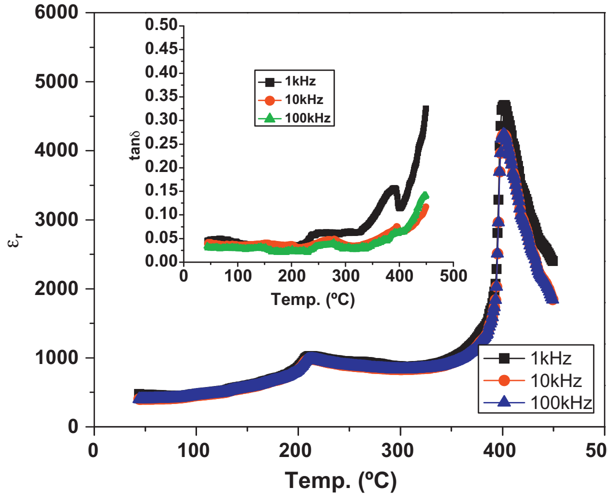

Fig. 4. Temperature dependence of dielectric constant of KNN sample. (Inset Fig. 4 temperature dependence of dielectric loss of KNN sample.)

The maximum value of ε_r at Curie temperature (T_c) at 1 kHz frequency is found to be ~4637. In perovskite type materials, ferroelectric to paraelectric phase transition occurs due to the instability of temperature dependent lowest frequency optical soft mode [20,21]. At T_c, the lowest frequency soft mode tends to zero and the lattice displacement associated with it becomes unstable. This leads to phase transition from ferroelectric to paraelectric region with max. ε_r at T_c, which can be explained by Lyddane–Sachs–Teller (LST) relation. The LST relation is given by,

$$\frac{\omega_T^2}{\omega_L^2} = \frac{\varepsilon(\infty)}{\varepsilon(0)} \qquad (1)$$

Here static dielectric constant ($\varepsilon(0)$) increases when the transverse optical (ω_T) phonon frequency decreases. Therefore, the higher values of ε_r near T_c is due to the condensation of soft mode frequency ($\omega_T \rightarrow 0$) [22]. The higher value of ε_r near T_c is also supported by the Curie weiss relation.

The inset Fig. 4 shows the temperature dependence of the dielectric loss (tan δ) at different frequencies of oxygen sintered KNN sample. The behavior of tan δ is very much similar to ε_r i.e. two similar kind of transition peaks are also observed here. It is observed that a higher value of tan δ is obtained with increasing temperature which may be due to the increase in the mobility of ions and imperfections in the material [23]. The RT tan δ value at 1 kHz frequency is found to be ~0.041. It can also be seen form Fig. 4 that the temperatures of peak dielectric loss and peak dielectric constant do not coincide. Kramers–Kronig relation indicates that this can be the consequence of temperature dependent relaxation near Curie temperature [24].

Fig. 5 shows the bipolar polarization vs electric field (*P*–*E*) hysteresis loops as a function of no. of switching cycles of KNN samples. The development of well saturated hysteresis loop confirms the ferroelectric nature of the material. It can also be noticed that the KNN samples exhibits fatigue behavior i.e. the spontaneous and remnant polarizations (P_r) are found to decrease by 11% with increase in switching cycles. It is known that bipolar fatigue generates microscopic defects and defect clusters in bulk samples, effectively pinning 90° domain wall motion, resulting in the loss of the value of P_r during continuous electric field switching [25]. The inset Fig. 5 shows the remnant

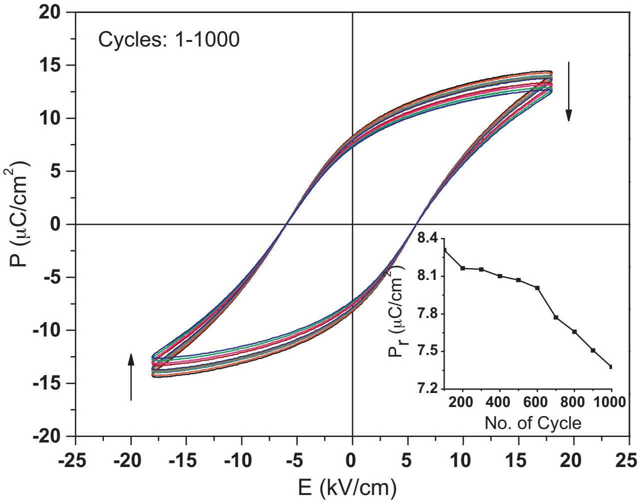

Fig. 5. Polarization vs electric field (*P–E*) loop of KNN sample. (Inset Fig. 5 shows normalized polarization vs switching cycle.)

polarization as a function of switching cycle for KNN ceramic, where a logarithmic decay in the value of P_r with increase in switching cycle is observed. It is found that the value of P_r has decreased from 8.31 to 7.40 μC/cm^2 when the switching cycle has increased from 100 to 1000. The piezoelectric constant (d_{33}) of the ceramic was found to be 84pC/N, which is higher than the one reported by conventional process. This may be attributed to the observed higher value of d_{ex} and improved microstructure in the presence of oxygen environment since oxygen sintering facilitates the domain wall switching and give rise to higher piezoelectric properties with lower coercive field [26].

4. Conclusions

Pure and single perovskite phase KNN samples have been obtained at lower calcinations temperature (~450 °C) using urea as a fuel. The presence of urea enhances the rate of reaction as a result of which single phase is obtained at 450 °C. Dense and uniform distribution of grains is obtained by sintering the sample in the oxygen environment at 1120 °C for 2 h. The room temperature dielectric and piezoelectric properties of the KNN sample are found to be superior than the conventionally prepared KNN samples. The results in this study indicate that combustion synthesis of KNN samples can be an effective technique to synthesize ferroelectric materials at lower calcinations temperature. Moreover, sintering of the samples in the oxygen environment may help to reduce the grain growth and enhance the density of the samples, resulting in good electrical properties.

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Samples, Academic Press, New York, 1971, pp. 221–224.

[2] G. Haertling, Ferroelectric samples: history and technology, J. Am. Ceram. Soc. 82 (1999) 797–818.

[3] J.W. Waanders, Piezoelectric Samples-Properties and Applications, Philips Components, Eindhoven, 1991.

[4] M.D. Maeder, D. Damjanovic, N. Setter, Lead free piezoelectric materials, J. Electroceram. 13 (2004) 385–392.

[5] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead free piezosamples, Nature 432 (2004) 84–87.

[6] G.Z. Zang, J.F. Wang, H.C. Chen, W.B. Su, C.M. Wang, P.Q. Ming, J. Du, L.M. Zheng, S. Zhang, T.R. Shrout, Perovskite (NaK)(LiSb)–NbO_3 lead free piezosamples, Appl. Phys. Lett. 88 (2006) 212908.

[7] M. Matsubara, K. Kikuta, S. Hirano, Synthesis and characterization of $(K_{0.5}Na_{0.5})(Nb_{0.7}Ta_{0.3})O_3$ piezoelectric samples sintered with sintering aid $K_{5.4}Cu_{1.3}Ta_{10}O_{29}$, Jpn. J. Appl. Phys. 44 (2005) 6618–6623.

[8] Y. Guo, K. Kakimoto, H. Ohsato, Phase transitional behavior and piezoelectric properties of KNN-LN samples, Appl. Phys. Lett. 85 (2004) 4121–4123.

[9] J. Wu, Y. Wang, D. Xiao, J. Zhu, P. Yu, L. Wu, W. Wu, Piezoelectric properties of $LiSbO_3$-modified $(K_{0.48}Na_{0.52})NbO_3$ lead-free samples, Jpn. J. Appl. Phys. 46 (2007) 7375–7377.

[10] H. Takao, Y. Saito, Y. Aoki, K. Horibuchi, Microstructural evolution of crystalline-oriented $(K_{0.5}Na_{0.5})NbO_3$piezoelectric samples with a sintering aid of CuO, J. Am. Ceram. Soc. 89 (2006) 1951–1956.

[11] E. Hollenstein, M. Davis, D. Damjanovic, N. Setter, Piezoelectric properties of Li- and Ta-modified $(K_{0.5}Na_{0.5})NbO_3$ samples, Appl. Phys. Lett. 87 (2005) 182905.

[12] R.E. Jaeger, L. Egerton, Hot pressing of potassium–sodium niobates, J. Am. Ceram. Soc. 45 (1962) 209–213.

[13] R. Wang, R. Xie, T. Sekiya, Y. Shimojo, Y. Akimune, N. Hirosaki, M. Itoh, Piezoelectric properties of spark-plasma-sintered $(Na_{0.5}K_{0.5})NbO_3$–$PbTiO_3$ samples, Jpn. J. Appl. Phys. 41 (2002) 7119–7122.

[14] H.B. Yang, Y. Lin, J.F. Zhu, F. Wang, H.J. Luo, Low-temperature combustion synthesis of $NaNbO_3$ powders, Mater. Manuf. Process. 23 (2008) 489.

[15] K. Deshpande, A. Mukasyan, A. Varma, Direct synthesis of iron oxide nano powders by the combustion approach: reaction mechanism and properties, Chem. Mater. 16 (2004) 4896–4904.

[16] H. Yang, Y. Lin, J. Zhu, F. Wang, An efcient approach for direct synthesis of $K_{0.5}Na_{0.5}NbO_3$ powders, Powder Technol. 196 (2009) 233–236.

[17] X. Vendrell, L. Mestres, Optimization of the sintering conditions of the $[(K_{0.5}Na_{0.5})1-xLi_x]NbO_3$ system, Phys. Procedia 8 (2010) 57–62.

[18] 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, Mater. Lett. 61 (2007) 785–789.

[19] H.L. Dua, F.S. Tang, D.J. Liu, The microstructure and ferroelectric properties of $(K_{0.5}Na_{0.5})NbO_3$–$LiNbO_3$ lead-free piezoelectric samples, Mater. Sci. Eng. B 136 (2007) 165–169.

[20] L. Egerton, M. Dillon, Piezoelectric and dielectric properties of samples in the system potassium sodium niobate, J. Am. Ceram. Soc. 42 (1959) 438–442.

[21] W. Cohran, Crystal stability and theory of ferroelectricity, Adv. Phys. 9 (1960) 387–423.

[22] A.S. Kandari, A. Bhandari, A.A. Bauria, N.S. Panwar, Electrical properties of $Na_{1-x}K_xNbO_3(0.28 \leq x \leq 0.4)$, Ferroelectrics 386 (2009) 139–151.

[23] P. Kumar, S. Singh, O.P. Thakur, C. Prakash, T.C. Goel:, Study of lead magnesium niobate–lead titanate samples for piezo-actuator applications, J. Appl. Phys. 43 (2004) 1501–1506.

[24] M.E. Lines, A.M. Glass, Principles and Applications of Ferroelectrics and Related Materials, Clarendon Press, Oxford, 1977.

[25] S. Zhang, R. Xia, H. Hao, H. Liu, T.R. Shrout, Mitigation of thermal and fatigue behavior in $K_{0.5}Na_{0.5}NbO_3$-based lead free piezo samples, Appl. Phys. Lett. 14 (2008) 152904.

[26] N.M. Hagh, B. Jadidian, A. Safari, Property-processing relationship in lead-free (K,Na, Li) NbO_3-solid solution system, J. Electroceram. 18 (2007) 339–346.