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Effect of Ball Milling on the Electrical and Piezoelectric Properties of $(K_{0.485}Na_{0.485}Li_{0.03})(Nb_{0.96}Sb_{0.04})O_3$ Ceramics

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Abstract. : Recently, research in developing lead-free piezoelectric materials has been gaining much attention due to the environmental concern caused by highly toxic lead (Pb) present in the most widely used lead-based piezoelectric materials like PZT. Among the lead-free piezoceramics, $(K_{0.5}Na_{0.5})NbO_3$ - based ceramics are promising because of their relatively high Curie temperatures and large piezoelectric coefficients. In the present work, nanopowders of different particle sizes for the lead-free ceramic system $(K_{0.485}Na_{0.485}Li_{0.03})(Nb_{0.96}Sb_{0.04})O_3$ were prepared under different milling conditions by using Retsch PM100 high-energy ball mill in which the sun wheel and grinding jar rotate in opposite directions with speed ratio of 1:-2. The milling was performed for 1h, 5h, 10h, and 15h, fixing the speed at 300rpm. The average particle size of the milled powders, as determined from TEM images, was found to first decrease as the milling time increases from 1h to 10h and then increase as the milling time further increases to 15h. The anomalous increase in particle size with milling time from 10h to 15h could be a result of prolonged grinding when the particles start coalescing to form bigger particles by way of releasing the excess energy built up due to increasing microstrain and specific surface energy. The smallest average particle size of the milled powder observed was 8nm for milling duration of 10h, and the ceramics prepared from the same powder showed the optimum density (ρ) of $4.33g/cm^3$, room temperature dielectric constant (ϵ_{rt}) of 424 and piezoelectric charge coefficient (d_{33}) of 190pC/N.

Introduction

It has been over half a century now that the piezoelectric materials used in electronic industries have been dominated by the lead-based perovskite solid solution $(1-x) PbZrO_3-xPbTiO_3$ ¹. But owing to environmental concerns caused by the hazardous substance—lead, which occupies 60 weight % in PZT, numerous investigators have been giving efforts to develop environmental-friendly lead-free materials. During recent years, many lead-free materials have been proposed, which include $BaTiO_3$ (BT), $KNaNbO_3$, $BiNaTiO_3$ (BNT), BNT-BT, $(Ba_{0.95}Sr_{0.05})(Zr_{0.05}Ti_{0.95})O_3$ (BSZT)^{2,4,5}. Among all the lead-free piezoceramics, alkaline niobate ceramics based on the composition $K_{0.5}Na_{0.5}NbO_3$ (KNN) have been most promising and have gained much attention after a significant breakthrough achieved by Saito *et al* in the textured KNN ceramics with co-dopants of Li, Ta, and Sb, which showed d_{33} as high as 416 pC/N⁶. Even though the techniques used have limited industrial viability, such a research finding opens a new horizon of hope for developing a lead-free

counterpart of PZT. However while working with KNN, we are faced with numerous problems such as the need for special handling of the starting powders due to volatility of alkaline elements, high sensitivity of the properties to stoichiometry, and complex densification processes. One of the methods commonly used for improving densification as well as maintaining stoichiometry in KNN ceramics is to optimize the sintering parameters. The departure from the stoichiometry has considerable effect on the electrical and piezoelectric performance of KNN system. Furthermore, there are no standard JAPDS-ICDD files for KNN. As a result, crystallographic indexing is found inconsistent in literature. A number of studies have been carried out to improve the sinterability and electrical properties of KNN ceramics⁸⁻¹¹. The present work is an effort toward improving the densification process so as to improve the electrical and piezoelectric properties of the ceramic system by preparing it from Nano powders. The idea underlying this work comes from the fact that reduction in particle size enhances the driving force for sintering¹². In the present investigation, we therefore chose one KNN-based composition which has been reported to possess optimum piezoelectric properties, namely $(K_{0.485}Na_{0.485}Li_{0.03})(Nb_{0.96}Sb_{0.04})O_3$ (KNLNS). The dependence of dielectric and piezoelectric properties of the above mentioned ceramic composition on milling duration of the starting powder is reported in this paper.

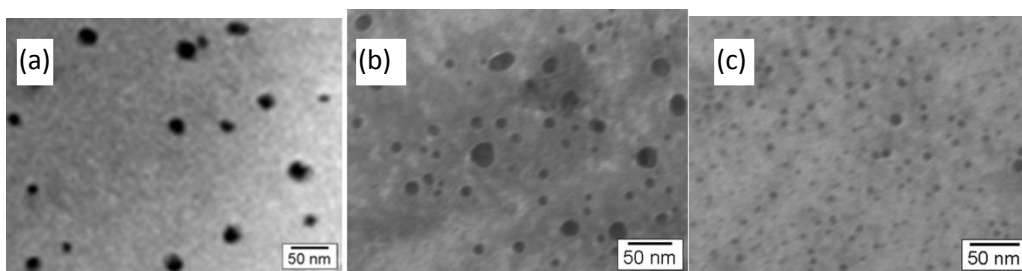
Experimental

The starting ingredients were AR grade with 99.9% purity powders of K_2CO_3 , Li_2CO_3 , Na_2CO_3 , Nb_2O_5 and Sb_2O_5 . The powders were homogeneously mixed in a ball mill using isopropyl alcohol as milling media along with zirconia balls. The mixture was dried and calcined for 3h at $900^\circ C$. The calcined powders were high energy milled in the isopropyl alcohol medium using a Retsch PM planetary ball mill in which the sun wheel and the grinding jar rotate in opposite directions with speed ratio 1:-2. Agate vial and balls were used. The milling was performed for different durations of 1, 5, 10, and 15h fixing the milling speed at 300rpm. During each high energy milling, a mass ratio of 1:5 for powder and balls was always maintained. The planetary ball mill was set to a rotational mode that changes the rotational direction of the vial and the sun wheel every 6 min after a rest interval of 2 min.

TEM (Morgagni 268) analysis was performed for studying the nature and size of the particles of the milled powders. X-ray Diffractometer (Discover S8) with monochromatic CuK_α radiation ($\lambda=1.54178\text{\AA}$) was used over 2θ angle ranging from 20° to 70° to determine the crystal structures of the milled powders. The bulk density of the sintered compacts was obtained by Archimedes method. For electrical measurements, silver paste was applied on both sides of the sintered samples as electrodes and fired at $200^\circ C$ for 1h. The dielectric constant 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 $100^\circ C$ 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).

Results and discussion

Figure 1 shows the TEM micrographs of the KNLNS powders milled for 1, 5, 10 and 15h at 300rpm. There is a clear evidence of changes in microstructure of the powders as the milling time increases from 1h to 15h. The average particle sizes of the milled powders as determined from the micrographs are given in Table 1. It is seen in this table that the particle size first decreases from 35nm to 8nm as the milling time increases from 1h to 10h and then increases to 15nm as the milling time further increases to 15h.



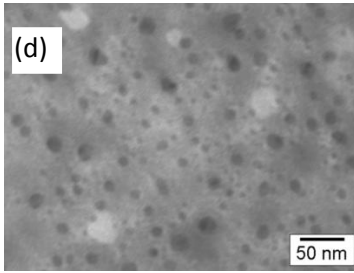


Fig. 1 TEM micrographs of KNLNS nanopowders produced by milling for (a) 1h, (b) 5h, (c)10h, and (d) 15h, at 300rpm.

As per the analytical model proposed by Gusev [13], the post milling particle size D of the powders depends upon the milling energy E_{mill} in the following way:

$$D = \frac{M[A + B \ln(D_{in} / 2b)\epsilon_{max} \{1 - \exp(ct)\}]}{E_{mill} + M[A + B \ln(D_{in} / 2b)\epsilon_{max} \{1 - \exp(ct)\}] / D_{in}} \quad (1)$$

where M is the mass of the initial powder, D_{in} their initial size, A and B are some constants characteristic of the material, b is the magnitude of Burgers vector associated with a disordered network of edge dislocations in the grains, the empirical function $\epsilon = \epsilon_{max}[1 - \exp(ct)]$ with $c < 0$ describes the dependence of the microstrains ϵ on the milling time t .

The milling energy E_{mill} provided to the powder is proportional to the cube of the angular rotation speed, ω^3 , and the milling time t , that is

$$E_{mill} = \kappa \omega^3 t \quad (2)$$

where κ is a constant parameter of the milling system.

Equation (1) can therefore be written as

$$D = \frac{M[A + B \ln(D_{in} / 2b)\epsilon_{max} \{1 - \exp(ct)\}]}{\kappa \omega^3 t + M[A + B \ln(D_{in} / 2b)\epsilon_{max} \{1 - \exp(ct)\}] / D_{in}} \quad (3)$$

Equation (3) predicts that, for a fixed ω , an increase in the milling time t should lead to a gradual decrease in the particle size D of the milled powder to a saturation value. Similar dependence of particle size on milling time t has also been predicted in other theoretical model¹⁴. In the present work, the decrease in average particle size from 35nm to 8nm as the milling duration increases from 1h to 10h agrees with these theoretical predictions. However, the further increase in the particle size from 8nm to 15nm corresponding to the milling time range 10h - 15h could not be understood on the basis of these theories. The observed trend of particle size variation with milling time has also been reported in other system¹¹. It is suggested that when we mill the powder for longer duration, a critical condition of instability is attained due to which smaller particles coalesce to form bigger particles in a process of releasing excess energy built up during milling. The surplus energy in the smaller particles derives its origin from the increasing specific surface energy of the particles consequent upon their size reduction to nanoscale region and the microstrains produced in the particles on account of their impacts with the milling media.

The XRD profiles for the KNLNS milled powders are shown in Fig. 2. It can be seen from this figure that the powder samples crystallize into pure perovskite phase. This suggests that Li^+ occupy A site and Sb^{5+} occupy B site in the lattice to form homogeneous solid solution. All the peaks in XRD patterns correspond to KNbO_3 structure in the ICDD database with JCPDS No. 71-0946 since it is isostructural with KNN. The crystal structure possesses orthorhombic symmetry specified by the splitting of (022) and (200) peaks.

The lattice parameters a , b and c , and unit cell volume V calculated from the XRD data analysis of KNLNS powders, versus milling speed are shown in Fig. 3a. All these parameters nearly follow a decreasing trend with the increase of milling duration, indicating thereby that ball milling of KNLNS powders results in a change in the size of the unit cell of the lattice. In addition, there is a noticeable change in the shape of the unit cell as indicated more clearly by the tetragonality (c/a) plot of Fig. 3b. As seen in this figure, the tetragonality increases with milling time till it reaches a maximum at 10h.

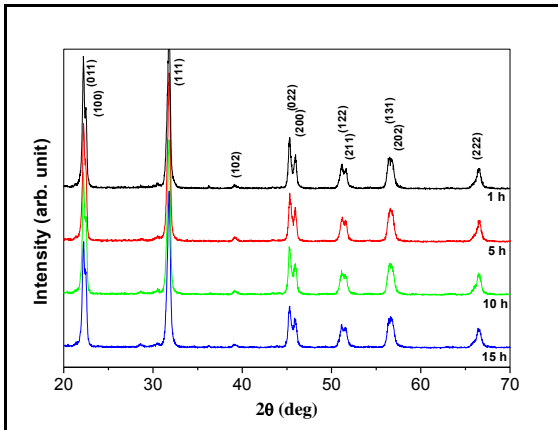


Fig. 2 Typical XRD pattern of KNLNS ceramics sintered at 1070°C for 3h

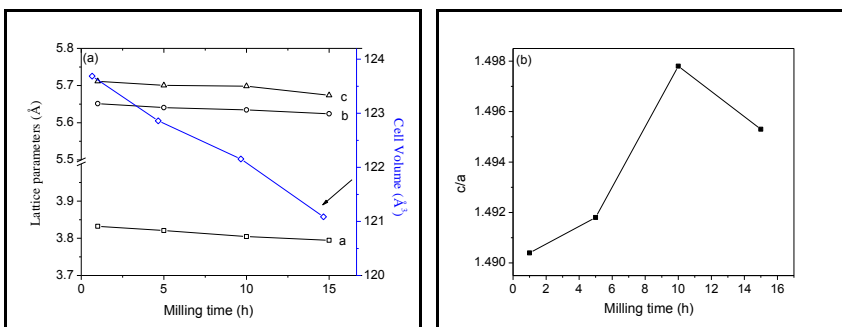


Fig. 3 Dependence of (a) lattice parameters and cell volume, and (b) c/a , on milling duration for KNLNS milled powders sintered at 1070°C for 3h.

Results in Fig. 3 thus reveal that there is a strong influence of milling duration of the high-energy ball mill on the shape and size of the crystal structure evolved in the powders.

The room temperature dielectric constant measured at 100 kHz for the KNLNS ceramics and the piezoelectric charge coefficient d_{33} for the poled samples are given in Table 1. The variation of the dielectric constant of the ceramics is in accordance with that of the observed density of the ceramics. The ceramics show an increase in both density and room temperature dielectric constant with increase in milling duration, peaking at 10h and then decreasing again with increase in milling hours. Thus the ceramic with highest density has the greatest room temperature dielectric constant. The change observed in d_{33} is also consistent with the corresponding changes in density and room temperature dielectric constant of the ceramic system. The ceramic prepared from 10h milled powder shows a d_{33} value of 190pC/N.

Table 1: Various properties of $(\text{K}_{0.485}\text{Na}_{0.485}\text{Li}_{0.03})(\text{Nb}_{0.96}\text{Sb}_{0.04})\text{O}_3$ ceramics

Milling time (h)	1	5	10	15
Initial particle size (nm)	35	20	8	15
Bulk density (g/cm^3)	4.16	4.22	4.33	4.27
Dielectric constant, ϵ_{rt}	376	382	424	399
d_{33} (pC/N)	120	145	190	178

The increased piezoelectric property observed in the ceramic prepared from 8-nm powder is attributed to a cumulative effect of density increase and higher tetragonality. As reported recently, the best piezoelectric properties in KNL–NTS piezoceramics are obtained for tetragonal symmetry, and therefore a linear correlation exists between tetragonal distortion and the piezoelectric properties^{15,16}. From this perspective, the development of KNN-based ceramics with a high tetragonal distortion could also be favorable for enhancing their piezoelectric properties.

Conclusion

Lead-free nanocrystalline $(K_{0.485}Na_{0.485}Li_{0.03})(Nb_{0.96}Sb_{0.04})O_3$ powders were prepared using conventional solid state reaction accompanied by high energy ball milling. The result on milling shows that the average particle size of the milled powders decreases with increasing milling time till it increases after reaching a critical value. The study reveals that KNN-based ceramics with superior properties can be prepared from nanopowders without the need for any sintering agents. The KNLNS ceramic prepared from the smallest 8-nm particles (corresponding to milling time of 10h) using normal air sintering method possesses optimum properties with room temperature dielectric constant of 424 and d_{33} value of 190pC/N.

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