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Dependence of Dielectric Properties on Sintering Conditions of Lead Free KNN Ceramics Modified with Li-Sb

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***Abstract*—**In order to produce lead free piezoceramics with optimum piezoelectric and dielectric properties, KNN modified with Li^+ (as an A site dopant) and Sb^{5+} (as a B site dopant) $(K_{0.49}Na_{0.49}Li_{0.02})$ $(Nb_{0.96}Sb_{0.04})$ O_3 (referred as KNLNS in this paper) have been synthesized using solid state reaction method and conventional sintering technique. The ceramics were sintered in the narrow range of 1050°C-1090°C for 2-3 h to get precise information about sintering parameters. Detailed study of dependence of microstructural, dielectric and piezoelectric properties on sintering conditions was then carried out. The study suggests that the volatility of the highly hygroscopic KNN ceramics is not only sensitive to sintering temperatures but also to sintering durations. By merely reducing the sintering duration for a given sintering temperature we saw an increase in the density of the samples which was supported by the increase in dielectric constants of the ceramics. And since density directly or indirectly affects almost all the associated properties, other dielectric and piezoelectric properties were also enhanced as we approached towards the most suitable sintering temperature and duration combination. The detailed results are reported in this paper.

***Keywords*—**Piezoceramics, Conventional Sintering, KNN, Lead Free.

I. INTRODUCTION

IT has been over a half century now that the electronic industries have been dominated by the piezoelectric ceramics based on the perovskite solid solution $(1-x)PbZrO_3$–$xPbTiO_3$, commonly referred to PZT [1]. But owing to environmental concerns caused due to hazardous substances of which lead is one of the leading members, numerous investigators have been developing alternative materials to PZT ceramics as it contains 60 weight % of lead in it. All these years, many lead free materials have been proposed, like- $BaTiO_3$ (BT) [2], $KNaNbO_3$ [3], $Bi_{0.5}Na_{0.5}TiO_3$ [4], $(Bi_{0.5}Na_{0.5})TiO_3$-$BaTiO_3$ [5], $(Ba_{0.95}Sr_{0.05})(Zr_{0.05}Ti_{0.95})O_3$ [6]. But among all the lead-free piezoceramics candidates, alkali niobate ceramics based on $K_{0.5}Na_{0.5}NbO_3$ (KNN) have been most promising [3], [7] and have seeked major attention after a massive breakthrough obtained by Saito et al. in the textured KNN ceramics with co-dopants of Li, Ta, and Sb, which shows a d_{33} constant as high as 416 pC/N [8]. Even though such techniques used, limit the industrial viability of the ceramics made but at least such a research opens a new horizon altogether for all the researches worldwide who are trying rigorously so as to produce a lead free counterpart for PZTs. However while working with KNN, we are faced with numerous problems such as (a) need for special handling of the starting powders due to volatility of alkaline elements, (b) high sensitivity of the properties to stoichiometry, and (c) complex densification processes. One of the ways is to optimize the sintering parameters, this is not only important for densification but also for controlling composition of the ceramics. The change of phase structure and the deviation of composition have considerable effect on the performance of various electrical properties. Furthermore, there are no standard JCPDS-ICDD files for KNN. As a result, crystallographic indexing is inconsistent in almost all the literatures. As reported by many earlier works, it has been confirmed that the major contribution to the high performance of KNN based piezoelectric ceramics depends upon controlling the sintering parameters. Hence, in this work we have studied the effect of sintering parameters on KNN ceramics modified with Li and Sb. Here, we would like to mention that along with sintering temperature, the duration of sintering also plays an equally important role and in this work we have brought this into focus. The detailed results are reported in this paper.

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II. EXPERIMENTAL PROCEDURE

Lead free KNLNS ceramics were synthesized by normal solid state reaction method using high purity (>99%) K_2CO_3, Na_2CO_3, Li_2CO_3, Nb_2O_5, Sb_2O_5 powders. Due to the highly hygroscopic nature of the alkali and carbonate powders, they were systematically dried at 200°C for 2 h before using. The measuring of these precursors was done using digital weighing balance (RS 22) according to the desired composition. The measured powders were then homogenized at first by ball-milling in isopropyl alcohol for 15 h and then in order to obtain a homogeneous mixture of the powder it was ball milled again in Retsch PM 100 planetary high energy ball mill for 1 h at a rate of 300rpm. After ball milling, the powder was dried in a digital oven at 70°C and then the dried powder was calcined in alumina crucibles at 900°C for 3 h.

The calcined powders were again ball milled in high energy ball mill for 5 h at a rate of 300rpm and then dried in oven for 4 h at a low temperature of 70°C. In order to proceed for sintering, the powders were then mixed with polyvinyl alcohol (binder) and granulated thoroughly in order to obtain a homogeneous mixture, and then they were pressed into disks (diameter 10mm) using hydraulic press. The pellets prepared were sintered at various temperatures ranging from 1050°C to 1090°C for 2-3 h. The samples were arranged in two batches. Sintering temperature for both the batches were identical, but batch1 was sintered for 3 h and batch 2 was sintered for 2 h. The comparative study of piezoelectric, dielectric and micro structural of these batches was then carried out in the following way. The densities of the sintered pellets were measured by Archimedes Principle. The crystal structure of the sintered specimens was studied using X-ray Diffractometer (Philips Diffractometer PW 3020) with monochromatic CuK_{α} radiation (λ=1.54178Å) over a 2θ angle from 20° to 70°. In order to perform electrical characterization, silver electrodes were fired on the pellets at 150°C for 1 h. Specimens for piezoelectric measurements were poled for 30 min in 120°C silicone oil bath by DC electric field of 3 kV/mm. The dielectric properties were measured by a LCR meter (ANDO 4304). The planar electromechanical coupling coefficient k_p and the mechanical quality factor Q_m were calculated by the resonance-anti resonance method using an impedance analyzer (Wayne Kerr 4294A). The piezoelectric constant d_{33} was measured using a Piezo d_{33} meter (YE2730A d_{33} METER).

III. Results and Discussions

Fig. 1 shows the X-ray diffraction pattern of 2mol% Li^+ doped $(K_{0.5}Na_{0.5})$ $(Nb_{0.96}Sb_{0.04})$ O_3 (KNNS) ceramics sintered under various sintering conditions. Just like the pure KNN ceramic, the ceramics prepared by us also possess perovskite structure with orthorhombic symmetry at the room temperature. $(K_{0.5}Na_{0.5})_{0.98}Li_{0.02}$ $Nb_{0.96}Sb_{0.04}O_3$ ceramics possess a single perovskite structure suggesting that Li and Sb have diffused into the KNN lattices to form a homogeneous solid solution without any detectable secondary phase. The XRD pattern was indexed by JCPDS no. 71-0946 in the ICDD database. The orthorhombic symmetry of the ceramics at room temperature is quite evident with the splitting of the peaks (022) and (200). A detailed picture is shown in Fig. 1 (b) with enlarged view of 2θ from 44°-47°. The lattice parameters (calculated using Cellcalc Software) decreased with the increasing sintering temperature giving rise to shrinkage in unit cell volume.

Fig. 2 shows the change in the sintered density of KNLNS ceramics as a function of sintering temperature. When the sintering temperature increased from 1050°C to 1080°C, the bulk density gradually increased from 3.74g/cm^3 to 4.38g/cm^3. Then when we further increased the temperature, we saw decrease in the density value. The low density values of the ceramics can be attributed to the highly volatile nature of the alkali members present in the composition which probably leads to a decrease in weight of the samples. The improved density of the ceramics sintered at 1080°C for 2 h is supported by the SEM images of the ceramics sintered at different sintering conditions which is shown in Fig. 3. As we approach the optimum sintering condition, grain growth occurs and hence compactness in the grains grows which promotes densification. On further increasing the temperature, as we can see grain size decreases giving rise to pores which could be responsible for lower density values at high sintering temperature.

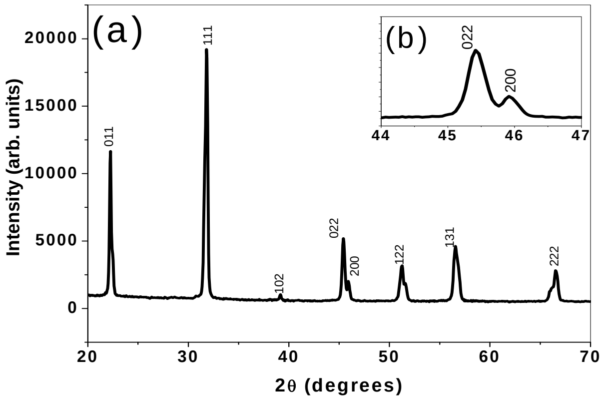

Fig. 1 X-ray diffraction pattern of crystal $(K_{0.49}Na_{0.49}Li_{0.02})$ $(Nb_{0.96}Sb_{0.04})$ O_3 sintered at 1080°C for 2 h. (a) XRD pattern for 2θ ranging from 20°-70° (b) enlarged pattern from 2θ 44°-47°

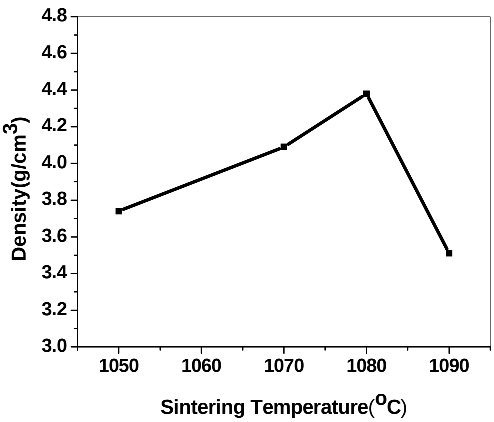

Fig. 2 the density dependence on sintering conditions for KNLNS ceramics. Samples were sintered for 3 h for temperature 1050°C, 1070°C, 1090°C and 2 h for temperature 1080°C

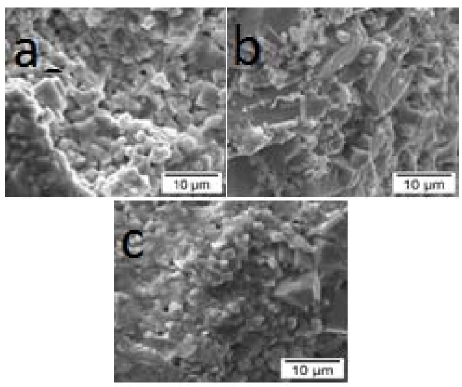

Fig. 3 SEM images of the ceramics sintered at different sintering conditions

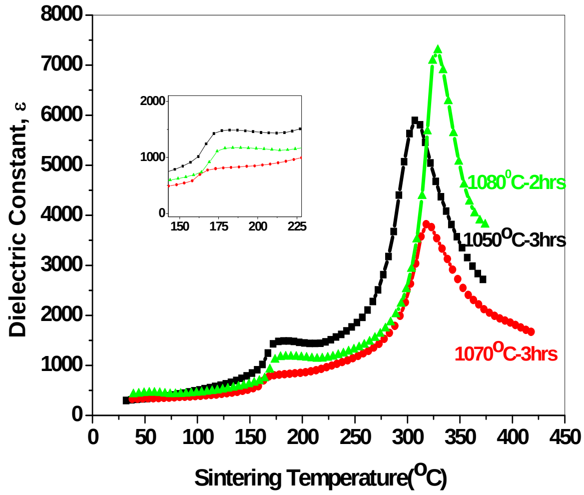

Fig. 4 Dependence of dielectric constant (ε) on temperature (measured at 100 kHz) for KNLNS ceramics

The temperature dependence of dielectric for KNLNS samples sintered at temperatures 1050°C (3 h), 1070°C (3 h) and 1080°C (2 h) measured at 100 kHz is shown in Fig. 4. In agreement with the earlier reported works, the dielectric V/s temperature curve for KNLNS ceramics also evidenced two phase transitions, i.e., Curie temperature (T_c) and orthorhombic to tetragonal transition temperature (T_{ot}). The curie temperature (T_c) shifted to higher temperatures as we approached the optimum sintering condition. The T_c of the ceramics ranges from 307°C-330°C. The high increase in value of T_c up to 22°C may be attributed to the fact that since Na^+ is more volatile than K^+, as we increase the temperature the percentage of K increases in the composition. This leads to an increase in T_c as we know that curie temperature of $KNbO_3$ is higher than that of $NaNbO_3$ It was earlier reported in many works that the partial substitution of $(NaK)^+$ ions with Li^+ increases the curie temperature whereas that of Nb^{5+} with Sb^{5+} decreases it [9]-[12]. Since we did not see very high values of T_c as reported in the previous mentioned literatures, it may be concluded that the effect of Sb dominated the effect of Li. The orthorhombic to tetragonal transition temperature T_{ot} also increased slightly towards the optimum sintering conditions. The T_c value reported in this paper coincides with many previous works including those which had the most similar composition to this work [13] but T_{ot} of the present ceramics did not show close values. The T_{ot} reported in this paper is quite high as compared to the above mentioned compositions. This could be due to presence higher of percentage of Sb^{5+} than Li^+ unlike the previous works. The decreased transition temperature values as compared to that of pure KNN also ensures that the Li and Sb have been absorbed by the KNN matrix.

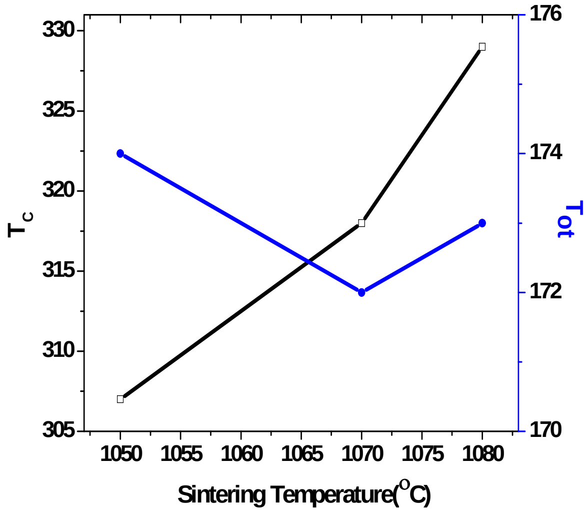

Fig. 5 Critical temperatures (T_c) and T_{ot} versus sintering temperature curve

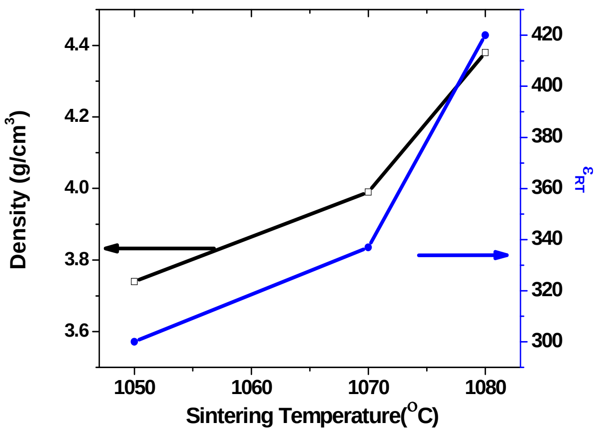

Fig. 6 Density and Dielectric constant at room temperature versus sintering temperature

The room temperature dielectric constant increases as we move towards the optimum sintering condition. This may be attributed to the fact that dielectric constant depends upon the density and since in this work density increases as we approach towards the optimum sintering condition, the corresponding dielectric constant also increases. The dependence of room temperature quality mechanical factor (Q_m) and dielectric loss (tan δ) on sintering condition is given in Table I. The quality mechanical factor decreased with rise in temperature for the ceramics sintered under conditions other than the optimum one. But for ceramics sintered at 1080°C for 2 h, Q_m rose up to a temperature of ~300°C and then decreased. On the other hand, the dielectric loss showed increased values with rise in temperatures for the ceramics not sintered under optimum conditions. But for ceramics sintered under optimum conditions tan δ remained in the range of 2-7% in the range of room temperature to high temperature up to ~300°C. The dielectric properties of the ceramic is summarised in Table I.

TABLE I
DIELECTRIC PROPERTIES OF KNLNS

Sintering Condition	Density	ε_{rt}	T_c	T_{ot}	Q_m	tan δ	ε_{max}
1050°C – 3 h	3.74	300	307	174	12.82	0.077	5899
1070°C – 3 h	3.95	337	318	172	15	0.065	3825
1080°C – 2 h	4.38	420	329	173	13	0.07	7294

Table I shows dielectric properties of KNLNS ceramics sintered at various sintering conditions.

IV. CONCLUSION

In the present work, we have studied the sintering behavior of Li^+ and Sb^{5+} modified KNN ceramics which are considered to be the most suitable replacement for PZTs. In this work, we have shown how sintering temperature and duration both affect the densification, dielectric and piezoelectric properties of KNN ceramics. Pure KNN ceramics were modified with 3 mol % of Li^+ and 4 mol % of Sb^{5+}, and detailed study of the dielectric properties of the $(K_{0.485}Na_{0.485}Li_{0.03})(Nb_{0.96}Sb_{0.04})O_3$ ceramics has been carried out in this work. The main focus of this work was to study the dependence of the properties of the ceramics on the sintering conditions. The properties such as T_c, ε_{rt}, ε_{max}, Q_m, tan δ tend to increase as we approach to the narrow sintering range. Also, the sintering temperatures used are low as compared to the high sintering temperatures used in some previous works. Dielectric loss (tan δ) was found to be very low for high temperatures which are a very important factor for high temperature applications.

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