



Influence of Calcination Kinetics Parameters on Synthesis of KNN Piezoelectric Ceramics

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ABSTRACT

The current research was focused on optimization of process parameters for synthesizing potassium sodium niobate (KNN) nano powders for the system $(K_{0.48}Na_{0.52})NbO_3$ by high energy ball milling process for 15h at a speed of 300 rpm and to evaluate the effect of calcination kinetics parameters on the synthesized KNN piezoelectric ceramics. Hence, blended KNN powders were calcined in conventional box furnace at 700°C, 800°C and 900°C for 5h, 7h and 10h. X-ray Diffraction results of the calcined powder confirmed the formation of pure perovskite structure at 900°C, 7h along with the phase transformation from orthorhombic to tetragonal crystal structure but resulted in the formation of secondary phases at 900°C, 10h. The study and analysis of calcination kinetics confirmed that solid state reaction was completed at 900°C, 7h without the formation of secondary phases. Fourier Transmittance Infra-Red Analysis (FT-IR) was carried out for 700°C, 800°C and 900°C to obtain the adsorption or emission of KNN nano powders and identified the stable crystal structure at 900°C, 10h. Morphology of the calcined powders revealed cubic structure with good compactness for 900°C, 10h with the particle size ranging from 65nm-120nm. The estimated crystallite size from Scherrer's equation using X-ray diffraction results was in the range of 7.08 nm to 16.11nm. Energy Dispersion spectroscopy results of calcined KNN powder ensured the completion of solid state reaction at 900°C, 10h which was in agreement with the X-ray diffraction, FTIR, SEM and calcination kinetics. The density of the KNN ceramics sintered at 1080°C for 30min reached a maximum value of 4.19g/cm³. KNN ceramics sintered at an optimum temperature of 1080°C exhibited piezoelectric properties, that is 125pC/N for d_{33} , 0.54 for K_p , 900.25 for Q_m , 12,800 for N_p (Hz. m).

1. INTRODUCTION

Piezoelectric materials are expected to acquire a market of around \$ 95 billion by 2017. Due to toxicity of Lead Zirconium Titanate [PZT] ceramics, its usage will end by 2017. So the recent research is concentrated on developing lead free piezo ceramics [1-7]. With this regard, two classes of lead free piezoelectric materials have drawn more attention, viz. bismuth layer structured ferroelectrics and perovskite structured ferroelectrics. Barium sodium titanate [BNT] based ceramics show large remnant polarization (38 μ C/cm²) but with a large coercive field (73kV/cm) [8] and a phase transition at 200°C from ferroelectric to anti ferroelectric. KNN is good compared to BNT due to its high Curie temperature. But achieving fully dense sodium-potassium based ceramics is difficult from normal sintering. Thus KNN powder has shown certain promising result which makes it a novel alternative for

lead based piezoelectric materials, if the synthesizing techniques and sintering path with various dopants can be optimized. Hence, challenges involved in processing of initial materials have to be addressed and calcination parameters have to be optimized to achieve enhanced piezoelectric charge constant and other coefficients.[9-13]

Fundamentally, there are two approaches to synthesize ceramic powders; mechanical and chemical methods. Out of this, ball milling method is best to get homogeneous ceramic powders of fine grain size with complete decomposition of carbonates and oxides without formation of complex oxides. It is also economically feasible on a large scale production. In chemical method, the existence of carbonates seen from thermal analysis is unavoidable and hard agglomerates may form which require grinding leading to contamination. [14-16]

Hence, the objective of the present work is to synthesize $(K_{0.48}Na_{0.52})NbO_3$ by high energy ball milling method and to optimize the milling hours to achieve homogenous nano crystalline KNN powders. This was

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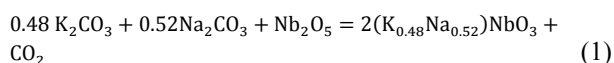
followed by the investigation of the crystal structure, phase transformation, absorption spectra, and elemental composition by optimizing and analyzing the calcination kinetics parameters and for achieving optimum rate and completion of solid state chemical reaction which is the key property to achieve high piezoelectric coefficient values.

2. MATERIALS AND METHOD

2.1. Starting Materials Sodium carbonate (Na_2CO_3) $\geq 99.5\%$, Niobium Pentoxide (Nb_2O_5) 99.9%, Potassium carbonate (K_2CO_3) $\geq 99.0\%$, were the initial raw materials used in this research and was purchased from Alpha Aesar, UK.

2.2. Ball Milling The stoichiometric composition for the system ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 was computed and the starting mixture was weighed accordingly and preheated at 200°C for 2h. Pre-heated mixture was then transferred to the steel vial of high energy ball mill with 10:1 BPR, 3-5 ml of acetone as processing reagent and milled at 300 rpm for 15h with a cycle time of 2h. After every 2h cycle, the lid of the vial was removed, cleaned and depending upon the adhesion of the blended powder to the vial or the ball, processing agent was added in the range of 0.2-0.5 ml until 15h of milling was completed.

2.3. Calcination The blended KNN powder was subjected to heat treatment process at 700°C , 800°C and 900°C for different time periods of 7, 8 and 10h. The chemical reaction that took place during the calcination process is as shown in equation (1).



Mass of the KNN nano-powder before and after heat-treatment process was measured to analyze the progress of the chemical reaction by computing the mass loss during calcination process which occurs due to the decomposition of carbonates into bi-carbonates and evolution of carbon-dioxide gas as an indication for completion of conventional solid state reaction. Calcination parameters were evaluated to optimize the feasible calcination temperature and duration to get the required perovskite structure, phase transformation and to overcome the formation of secondary phases / complex oxides. The calcined powder was mixed thoroughly with polyvinyl alcohol [PVA] solution and then pressed into disc of 10mm diameter and 1.5 mm thickness under 150Mpa pressure.

2.4. Sintering and electrical measurements

The Microwave sintering of the green samples was carried out at 1080°C for 30 minutes in air. The bulk densities of the samples were measured by the Archimedes principle using density meter. XRD

analysis of pellets was performed in order to examine the phase structure. Silver paste was applied on both sides of the samples for the electrical measurements. Electromechanical coupling coefficient (K_p), mechanical quality factor Q_m , frequency constant N_p , and dielectric constant (ϵ_r) were computed by measuring capacitance, impedance and dissipation factor from semiconductor device analyzer at 1kHz, 10kHz, 100kHz, 1MHz, 1.1MHz, 1.2MHz, 1.3MHz. The samples were polled in a silicon oil bath at 30°C , 100°C , 170°C , 185°C by applying dc fields of 3kV/mm for 30min for the measurement of peizo-electric properties. Peizo-electric charge constant of poled samples was determined by using peizo-meter system at 110Hz with proper aspect ratio.

2.5. Characterization XRD patterns of calcined ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 powders were recorded using Rigaku SmartLab X-ray diffractometer system with CuK_α radiation which was used to measure phase identification, crystallite size and chemical composition of the materials. The FTIR spectra of calcined KNN powder was graphed in linear array beginning with the wave-number 399.193 cm^{-1} using FT/IR – 4200 type A model with a scanning speed of 2 mm/s to obtain required spectra of absorption and transmittance of synthesized KNN powder. The morphology of the calcined KNN powder at 700°C , 800°C and 900°C for 10h was recorded by using Zeiss Supra-40 with scans of 100nm and 500nm to determine the shape and size of the particles. Fabricated green samples were densified using Micro Wave assisted Sintering furnace (MWAS) made by VB Ceramics. XRD patterns and morphology of sintered samples was recorded by using Rigaku SmartLab and Zeiss Supra-40, respectively. Semiconductor device analyzer, B1500A, Agilent technologies was used for electrical measurement. Peizo test d33 peizo meter system, Piezotest Pte. Ltd was used to determine peizo-electric charge constant.

3. RESULT AND DISCUSSION

3.1 X-Ray Diffraction of calcined powders

The comparison between the starting mixture and the blended mixture of KNN powders at 5, 10 and 15h is shown in Figure 1. The X-ray diffraction results of the initial mixture were heterogeneous in nature as it was not blended to achieve homogeneity. 5h milled powder showed increase in the intensity of the peak at 25° as an initiation for the formation of the perovskite structure. The minor peaks between 2θ values from 30° to 60° were associated with the remains of the starting powder which was heterogeneous in nature indicating that further milling of the powder is essential to achieve proper blending of the powder. The intensity of the minor peaks at 10h blended powder was comparatively less when compared with 5h blended powder diffraction

results indicating that the remnants of the starting materials is negligible. The nature of the peaks for 15h blended powder was similar to that of diffraction data at 10h blended KNN powder. So the milling hours was optimized to 15h in order to achieve homogeneity in blended KNN nano-powder.

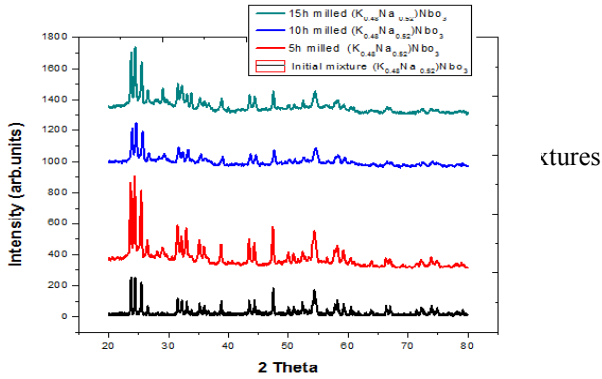


Figure 1. XRD patterns of blended $(K_{0.48}Na_{0.52})NbO_3$ powders associated with $700^\circ C$ at 5h, 7h and 10h are shown in Figure 2. Powders calcined at $700^\circ C$ depict homogeneous mixture with the formation of pure perovskite phase at (111) and (100) plane. This initiated for the formation of orthorhombic crystal structure at 2θ value in the range of $20-35^\circ$. But the intensity of the perovskite structure formed was not a dominant one and the phase transformation from orthorhombic to tetragonal crystal structure was not formed. The lattice parameters of $700^\circ C$, 10h calcined powders is indicated in TABLE 1. which shows the presence of both orthorhombic ($a \neq b \neq c$) and tetragonal ($a = b \neq c$) crystal structure with $\alpha = \beta = \gamma = 90^\circ$ but orthorhombic being dominant one. The unit cell parameters indicated the need for further calcination to make the tetragonal structure being the dominant one and to obtain the required phase transformation.

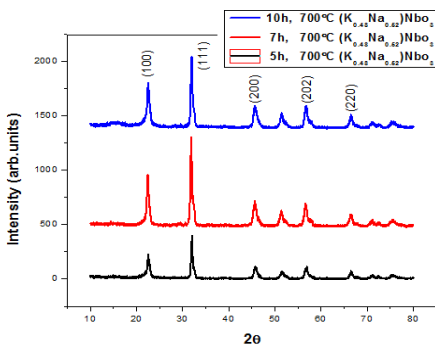


Figure 2. XRD patterns of calcined $(K_{0.48}Na_{0.52})NbO_3$ powders at $700^\circ C$ for 5h, 7h and 10 h.

The X-ray diffraction results of calcined KNN powders for $800^\circ C$ at 5h, 7h and 10h are indicated in Figure 3. The perovskite structure which emerged at $700^\circ C$ was

now pronounced in its intensity across the plane (011) and (002) for 2θ values ranging from $20-35^\circ$. The intensity of the minor peaks at 2θ values between $45-75^\circ$ laid the foundation for phase transformation to occur due to initiation of the peak split. The lattice parameters of $800^\circ C$, 10h calcined powders are listed in TABLE 2. which ensure tetragonal structure being dominant one as the lattice parameter at 2θ values satisfied ($a = b \neq c$), but non-visibility of phase transformation initiated for further heat treatment process to achieve pronounced peak split up and to obtain a dominant perovskite structure with required phase transformation.

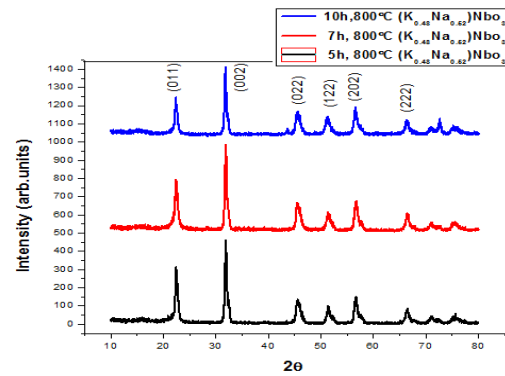


Figure 3. XRD patterns of calcined $(K_{0.48}Na_{0.52})NbO_3$ powders at $800^\circ C$ for 5h, 7h and 10 h.

TABLE 1. Unit cell parameters of $700^\circ C$, 10h Calcined $(K_{0.48}Na_{0.52})NbO_3$ powders.

No.	a [Å]	b [Å]	c [Å]	Alpha [°]	Beta [°]	Gamma [°]	Cell Volume [Å³]	Indexing M...	Not index.	FOM
9	10.7401	6.2940	5.8112	90.0000	90.0000	90.0000	392.8271	Treer	1	15.0000
6	11.2434	5.5352	3.2360	90.0000	90.0000	90.0000	201.3893	Treer	2	28.0000
4	6.3627	6.3627	11.8399	90.0000	90.0000	90.0000	479.3235	Treer	3	20.0000
8	11.9567	7.8928	4.0961	90.0000	90.0000	90.0000	386.5605	Treer	2	22.0000
11	10.7401	6.2940	5.8112	90.0000	90.0000	90.0000	392.8271	Treer	1	15.0000
7	8.4817	7.5075	5.5356	90.0000	90.0000	90.0000	352.4843	Treer	2	14.0000
3	5.6072	5.6072	12.4356	90.0000	90.0000	90.0000	390.9903	Treer	3	27.0000
2	3.9655	3.9655	12.4337	90.0000	90.0000	90.0000	195.5210	Treer	3	30.0000
10	10.7401	6.2940	5.8112	90.0000	90.0000	90.0000	392.8271	Treer	1	15.0000
1	6.2665	6.2665	17.2995	90.0000	90.0000	90.0000	679.3246	Treer	3	12.0000
5	15.9265	8.1378	5.9930	90.0000	90.0000	90.0000	776.7296	Treer	2	8.0000

TABLE 2. Unit cell parameters of $800^\circ C$, 10h Calcined $(K_{0.48}Na_{0.52})NbO_3$ powders.

No.	a [Å]	b [Å]	c [Å]	Alpha [°]	Beta [°]	Gamma [°]	Cell Volume [Å³]	Indexing M...	Not index.	FOM
10	5.6223	5.6223	4.0108	90.0000	90.0000	90.0000	126.7846	Treer	2	74.0000
11	3.9756	3.9756	8.0216	90.0000	90.0000	90.0000	126.7846	Treer	2	72.0000
12	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
13	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
14	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
4	3.9756	3.9756	8.0216	90.0000	90.0000	90.0000	126.7846	Treer	2	72.0000
5	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
6	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
7	10.2806	10.2806	8.7233	90.0000	90.0000	120.0000	798.4559	Treer	1	14.0000
8	3.9756	3.9756	4.0108	90.0000	90.0000	90.0000	63.3923	Treer	2	126.0000
9	5.6296	5.6296	3.9733	90.0000	90.0000	90.0000	125.9249	Treer	2	47.0000
3	5.6223	5.6223	4.0108	90.0000	90.0000	90.0000	126.7846	Treer	2	74.0000
2	5.6296	5.6296	3.9733	90.0000	90.0000	90.0000	125.9249	Treer	2	47.0000
1	3.9756	3.9756	4.0108	90.0000	90.0000	90.0000	63.3923	Treer	2	126.0000

The X-ray diffraction data of the calcined KNN powders for $900^\circ C$ at 5h, 7h and 10h is indicated in

Figure 4. The result depicts complete growth of the perovskite structure across the plane (012), (110) for 2θ value in the range of $20-35^\circ$ with full intensity. The peak split up was visible from $45-60^\circ$ which showed the presence of phase transformation from orthorhombic to tetragonal. The required transformation was associated with (024), (122) and (300) planes. There was no formation of secondary phase up-till $900^\circ\text{C}, 7\text{h}$ but resulted in the formation of minute complex oxides at $900^\circ\text{C}, 10\text{h}$. The lattice parameters of $900^\circ\text{C}, 10\text{h}$ calcined KNN powders are shown in TABLE 3. which ensure tetragonal structure being dominant one as almost all the lattice parameter for 2θ values satisfied ($a = b \neq c$).

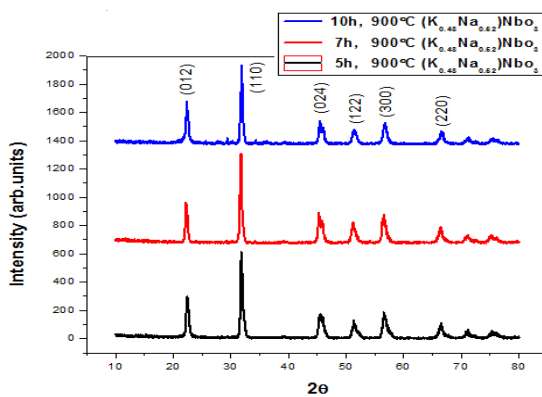


Figure 4. XRD patterns of calcined ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 powders at 900°C for 5h, 7h and 10h.

TABLE 3. Unit cell parameters of $900^\circ\text{C}, 10\text{h}$ Calcined ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 powders.

No.	a [Å]	b [Å]	c [Å]	Alpha [°]	Beta [°]	Gamma [°]	Cell Volume [Å ³]	Indexing M...	Not index...	FOM
1	6.9353	6.9353	14.3938	90.0000	90.0000	90.0000	692.3208	Tetror	3	13.0000
2	11.2388	11.2388	5.5369	90.0000	90.0000	90.0000	699.3749	Tetror	2	26.0000
3	15.7747	15.7747	3.9909	90.0000	90.0000	90.0000	993.1074	Tetror	3	40.0000
4	15.9033	15.9033	3.9429	90.0000	90.0000	90.0000	997.2232	Tetror	2	20.0000
5	11.2445	11.2445	3.9434	90.0000	90.0000	90.0000	498.5966	Tetror	3	36.0000
6	15.9685	7.7048	4.5828	90.0000	90.0000	90.0000	563.8395	Tetror	0	9.0000
7	12.5735	12.4609	2.7086	90.0000	90.0000	90.0000	424.3764	Tetror	1	28.0000
8	12.5430	12.5430	2.7044	90.0000	90.0000	90.0000	425.4792	Tetror	6	28.0000

Magnified view of the diffraction results of calcined KNN powders at 900°C for 5h, 7h and 10h was shown in Figure 5. Here the initiation for the peak split up was clearly visible at $900^\circ\text{C}, 5\text{h}$ which was sharp and pronounced at 5,7h respectively between 2θ values $45-60^\circ$, confirming the phase transformation from orthorhombic to tetragonal structure has taken place with tetragonal structure being dominant one at (122) and (300) planes.

Hence, the optimized calcination temperature established by diffraction result to achieve pure perovskite structure with phase transformation exclusive of secondary phases was $900^\circ\text{C}, 7\text{h}$.

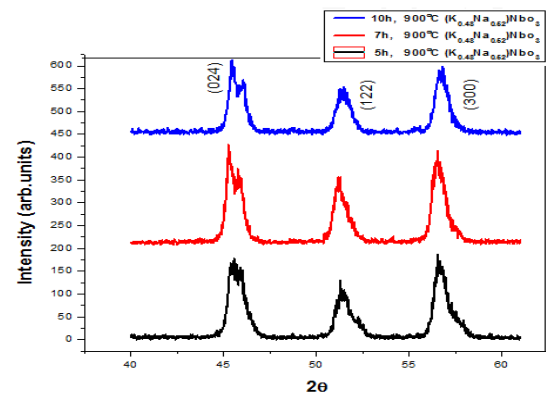


Figure 5. Magnified diffraction patterns for 5h, 7h and 10h at 900°C calcined ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 for 2θ value ($45-60^\circ$).

3.2. Calcination Kinetics

The calcination kinetics of KNN nano powders at 700°C for 5, 7 and 10h is shown in TABLE 4. Here the initial mass of the blended powder and the final mass of the calcined powder was determined. The percentage of mass loss for 5h of calcination process was comparatively less than that of 7h and 10h, indicating that the chemical reaction of the measured sample has started and is associated with removal of moisture as they are hygroscopic in nature. The mass loss of the calcined powders for 7h is maximum compared to powders calcined for 10h attributing for non persistent of hygroscopic components and decomposition of carbonates into bicarbonates. Mass loss for 700°C calcined powders for 10h indicated complete decomposition of carbonates and presence of carbon-dioxide still in the calcined powder resulting in the need for further calcination process.

TABLE 4. Calcination kinetics of ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 powders at 700°C

Calcination Period	Initial Mass (g)	Final Mass (g)	Mass Difference (g)	Mass Loss (%)
5h	0.8086	0.7105	0.0981	12.13
7h	0.8086	0.6628	0.1458	18.03
10h	0.8086	0.6809	0.1277	15.79

TABLE 5. Calcination kinetics of ($\text{K}_{0.48}\text{Na}_{0.52}$) NbO_3 powders at 800°C

Calcination Period	Initial Mass (g)	Final Mass (g)	Mass Difference (g)	Mass Loss (%)
5h	0.8086	0.6755	0.1331	16.46
7h	0.8086	0.6836	0.125	15.45
10h	0.8086	0.6921	0.1165	14.40

The calcination kinetics of KNN nano-powders at 800°C for 5, 7 and 10h is shown in TABLE 5. Here, the

initial mass of the blended powder and the final mass of calcined powder was determined. The percentage loss of mass for 5h calcination process was more comparative to 700 °C ensuring increased rate of removal for hygroscopic components. The mass loss of 7h calcined powders at 800°C was attributed to decomposition of alkaline bicarbonates [AHCO₃] to alkaline carbonates [ACO₃]. The mass loss of powders calcined for 10h at 800 °C is comparatively less which indicates complete decomposition of carbonates but the existence of carbon dioxide. As a result, the reaction is not 100% and still enhanced heat treatment process was essential for complete release of carbon-dioxide to achieve the required KNN system.

TABLE 6. Calcination kinetics of (K_{0.48}Na_{0.52})NbO₃ powders at 900°C.

Calcination Period	Initial Mass (g)	Final Mass (g)	Mass Difference (g)	Mass Loss (%)
5h	0.8086	0.6146	0.194	23.99
7h	0.8086	0.6273	0.1813	22.42
10h	0.8086	0.7645	0.0441	5.45

The calcination kinetics of KNN nano-powders at 900°C for 5, 7 and 10h is shown in TABLE 6. It provides the initial mass of blended powder and the final mass of the calcined powder. The percentage of mass loss after 5h of calcination was high ensuring maximum removal rate of hygroscopic compounds and initiation of decomposition of carbonates. The mass loss at 900°C for 7h calcination indicated successful formation of bicarbonates and the release of carbon-dioxide. Whereas the mass loss for 900°C calcined powders for 10h is much lower indicating almost complete release of carbon dioxide and ensuring completion of solid state reaction with the formation of (K_{0.48}Na_{0.52})NbO₃ powder.

3.2.1. Analysis of calcination Kinetics

Analysis of calcination kinetics of KNN powders at 700°C, 800°C and 900°C for different time periods of 5h, 7h and 10h is shown in TABLE 7. The calcined (K_{0.48}Na_{0.52})NbO₃ powders at 700, 800 and 900°C for 5h reveals that the removal rate of hygroscopic components and carbon dioxide gradually increased from 700°C to 800°C and is relatively high at 900°C heat treated powder.

Major mass loss of calcined powders was associated with 7h at 700°C, 800°C and 900°C, 5h calcined powders indicating decomposition of carbonate into bicarbonates. Mass loss of calcined powders for 10h at 900°C was the least confirming completion of the chemical reaction with release of carbon dioxide whereas mass loss at 700°C and 800°C is comparatively

more indicating that reaction is yet to be completed. Analysis of calcination parameters indicated that the curves of different temperature and duration was parabolic in nature and suggested that calcination at 900°C, 10h is the optimized heat treatment condition to synthesis KNN Nano powders with K/Na ratio of 0.48/0.52. But formation of secondary phases, which arise in the diffraction patterns [Figure 3.] at 900°C for 10h of calcination, restricted the feasible calcination time to 7h. Hence, suitable calcination condition to synthesize KNN Nano-powder is 900°C, 7h.

TABLE 7. Calcination kinetics of (K_{0.48}Na_{0.52})NbO₃ powders at 700-800°C and 900°C

Calcination temperature	% Mass loss at 5h	% Mass loss at 7h	% Mass loss at 10h
700° C	12.13	18.03	15.79
800° C	16.46	15.45	14.40
900° C	23.99	22.42	5.45

The calcination kinetics of KNN nano crystalline powder at 700°C, 800°C and 900°C for different time periods of 5h, 7h and 10h is shown in Figure 6. Percentage of mass loss vs. temperature curve of 700 °C attributes to be a non linear curve indicating chemical reaction was in progress with major mass loss associated at 7h of calcination attributing to 75% of the reaction to be completed at 7h. 800°C calcination plot with respect to time varied linearly at all duration without much mass loss ensuring chemical reaction was in progress and yet to be completed fully. This was accompanied by a non-linear curve at 900°C with insignificant mass loss at 10h ensuring major reaction was completed at 7h followed with remains of the reaction to be released across 10h of calcination temperature.

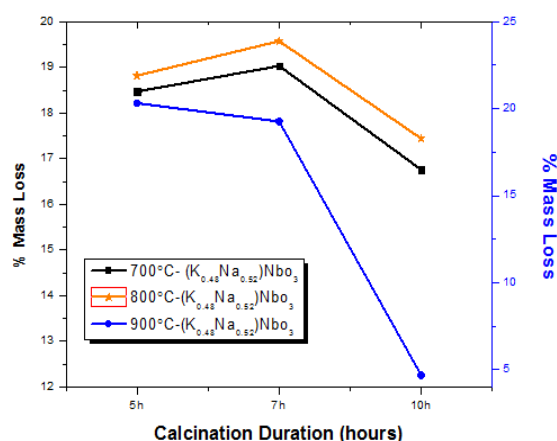


Figure 6. Analysis of calcination kinetics for (K_{0.48}Na_{0.52})NbO₃ powders for 700, 800 and 900°C C at 5, 7 and 10h.

Analysis revealed that the reaction rate at 700°C was higher for 7h in comparison with that of 5,10h calcination, followed with high reaction rate at 800°C and 900°C for 5h in comparison with 7 and 10h of calcination process ensuring the similarity in the reaction progress for 800°C and 900°C heat treatment processes. This analysis ensured that chemical kinetics is time and temperature dependant.

3.3. Fourier Transmittance Analysis of calcined powder

FTIR spectra of 700°C, 10h calcined KNN powder are as shown in Figure 7. The transmittance spectra reveals absorption bands at wave numbers 676.76 cm⁻¹, 1603 cm⁻¹ and 2928.4 cm⁻¹. The stretch at 676.76 cm⁻¹ ensures the existence of perovskite structure and corresponds to single bond between alkali metals and oxygen atoms i.e. Na - O - K, since the wave-numbers between 0 - 1550 cm⁻¹ are associated with single bonds. It can be inferred from Figure 7. that the percentage of absorbance at 676.76 cm⁻¹ was 24% (or transmittance being 76%). Absorption of 24 % of beam meant that for a given input beam of light, the electromagnetic radiation absorbed was less. The stretch at 1603 cm⁻¹ is attributed to R-CO₃-R¹CO₃ in particular K₂CO₃ Na₂CO₃, Nb₂O₅ as shown in Figure 7. The existence of these carbonates ensures that still complete solid state chemical reaction was not achieved in 700°C, 10h calcined powder. The absorption band at the wave-number of 2928.4 cm⁻¹ is associated with the single bonds of hydrogen (O-H, C-H) which are usually common in all organic compounds attributed to remains of carbonates and it could be ignored as it is lower than 3000 cm⁻¹ as shown in Figure 7. The presence of non-converted anhydride carbonates ensures that a stable crystal structure was not yet present completely in 700°C, 10h calcined KNN powder.

FTIR spectra of 800°C, 10h calcined KNN powder are as shown in Figure 8. The absorption bands revealed by the transmission spectra was indicated at wave numbers 684.34 cm⁻¹, 1628 cm⁻¹ and 2925.5 cm⁻¹. The stretch at 684.34 cm⁻¹ corresponded to single bond between the alkali metal atom and oxygen atom (O-R), in particular Na - O - K which depicted the existence of perovskite structure. It can be inferred from Figure 8. that the percentage of absorbance at 684.34 cm⁻¹ is 55% (or transmittance of 45 %) which shows the initiation of phase transformation from orthorhombic to tetragonal. The low percentage of absorption of 55 for a given input beam of light meant that a stable crystal structure was not present completely in 800°C, 10h calcined powder. The 1628 cm⁻¹ corresponding to double bonds indicated the presence of K₂CO₃, Na₂CO₃ and Nb₂O₅ anhydride material by 50%, followed with a minor stretch at 2925.5 cm⁻¹ which was associated with single bonds of hydrogen due to remains of carbonates of these organic compounds and it is treated to be negligible as it is nearer to 3000 cm⁻¹.

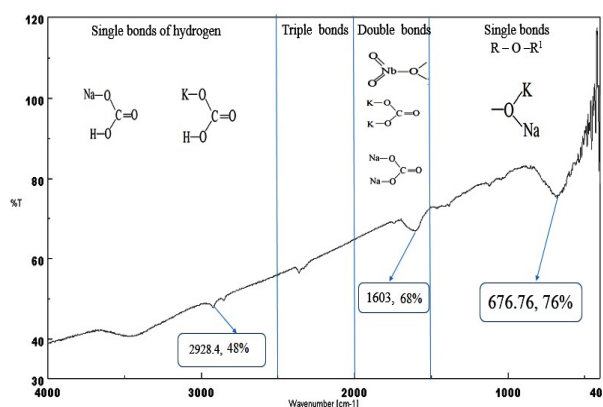


Figure 7. FTIR spectra of (K_{0.48}Na_{0.52})NbO₃ calcined.

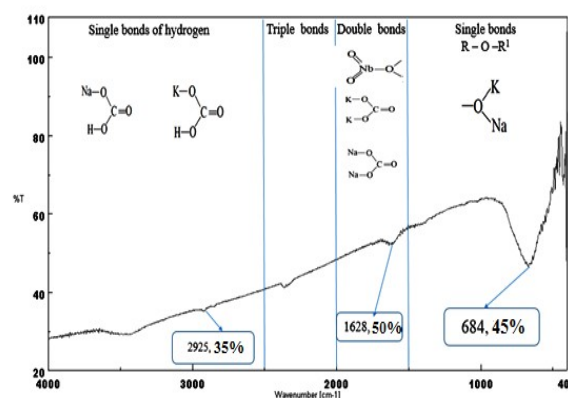


Figure 8. FTIR spectra of (K_{0.48}Na_{0.52})NbO₃ calcined powder at 800°C, 10h.

FTIR spectra of 900°C, 7h calcined KNN powder are as shown in Figure 9. The spectra indicated three absorption bands at wave numbers 666 cm⁻¹, 1595 cm⁻¹ and 2922.6 cm⁻¹. The wave number 666 cm⁻¹ corresponds to single bond between the alkali metal atom and oxygen atom (O-R) in particular Na-O-K which shows the existence of perovskite structure. It can be inferred from Figure 9. that the percentage of absorbance at 666 cm⁻¹ is 68 % (or transmittance of 32 %). Absorption of 68 % of a given input beam of light meant that the beam absorbed by the material was enhanced. This indicated that stable crystal structure was formed in 900°C, 7h calcined powder. The 1595 cm⁻¹ absorbance corresponds to double bonds indicating the presence of K₂CO₃ and Na₂CO₃ anhydride material by 42%, followed with a small stretch at 2925.5 cm⁻¹ which is attributed to minute remains of carbonates. The deep stretch at 666 cm⁻¹ ensured the formation of stable (K_{0.48}Na_{0.52})NbO₃ nano-powders at 900°C, 7h which was in agreement with X-ray diffraction and calcination kinetics results of KNN powder.

3.4. Morphology of calcined KNN powder

The morphology of calcined powder at 700°C, 10h with

scan of 100nm is shown in Figure 10. Microstructure at 700°C revealed loose compactness of the calcined KNN nano powders with cubic crystal structure accompanied by more pores emphasising that further heat treatment process is essential to obtain better compactness. The particle size was in the range of 69nm to 134nm. The morphology of calcined KNN powder at 800°C, 10h is shown in Figure 11. Morphology describes better compactness and reduced pore size in comparison with 700°C microstructure followed with cubic structure with improvement in the particle size of calcined powder ranging from 94nm to 124nm.

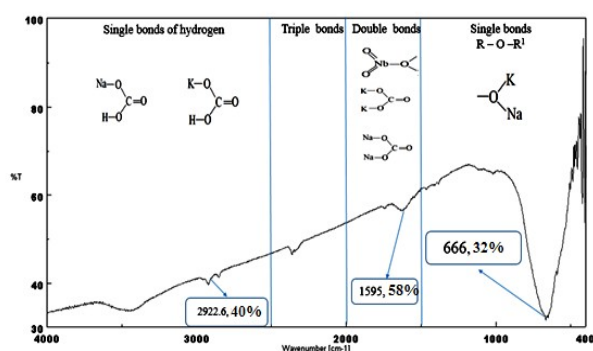


Figure 9. FTIR spectra of $(K_{0.48}Na_{0.52})NbO_3$ calcined powder at 900°C, 10h

The morphology of calcined powder at 900°C, 10h is shown in Figure 12. The microstructure revealed good compactness and reduced pore size with homogeneous crystal growth in comparison with 700°C and 800°C micro-structural results with grain size ranging from 71.80nm- 135nm with cubic crystal structure ensuring required grain growth of the calcined KNN nano powders which was in agreement with diffraction results at 900°C, 10h.

3.5. Computing crystallite size of calcined KNN nano crystalline powder

The grain size of KNN nano-powders were computed from diffraction results of calcined powders at 700°C, 800°C and 900°C by applying Scherrer's mathematical relation as shown in equation 2, where D_V is grain size, λ is the wavelength of x-ray, β is the line broadening at half of the maximum intensity (FWHM), θ is the angle of diffraction and k is shape factor close to unity having typical value between 0.8-0.9.

$$D_V = \frac{k \times \lambda}{\beta \times \cos \theta} \quad (2)$$

The evolution of grain size, just as an operation at different calcination temperatures and durations, is shown in Figure 13. The grain size increases from 7.082nm \pm 0.22nm (700°C) to 16.112nm \pm 0.25 nm (900°C). Also crystallite size and its dispersion increased linearly and became saturated across 900°C, 7h

attributing to parabolic in nature. 700°C curves depict rapid increase in the crystallite size (7.082 \pm 0.22 nm to 9.974 \pm 0.49 nm) demanding the need for higher calcination temperature.

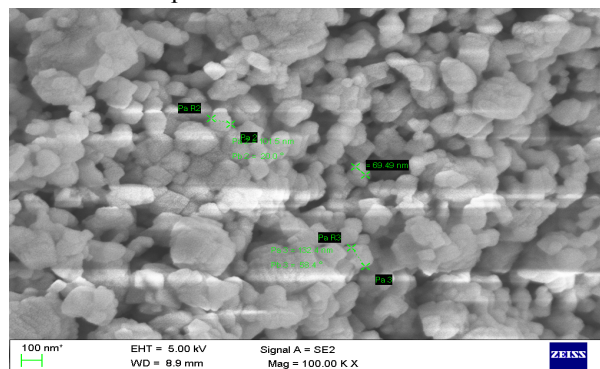


Figure 10. Morphology of $(K_{0.48}Na_{0.52})NbO_3$ calcined powders at 700°C, 10h.

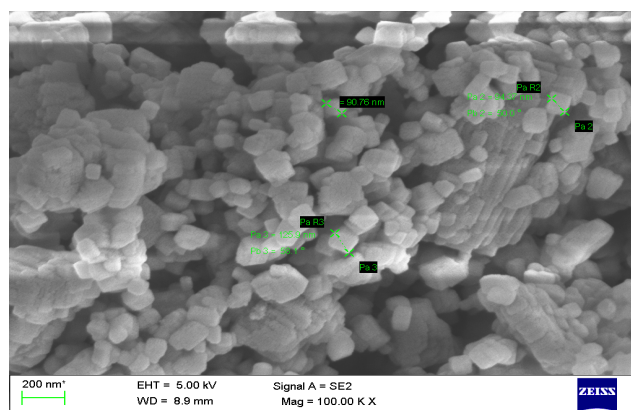


Figure 11. Morphology of $(K_{0.48}Na_{0.52})NbO_3$ calcined

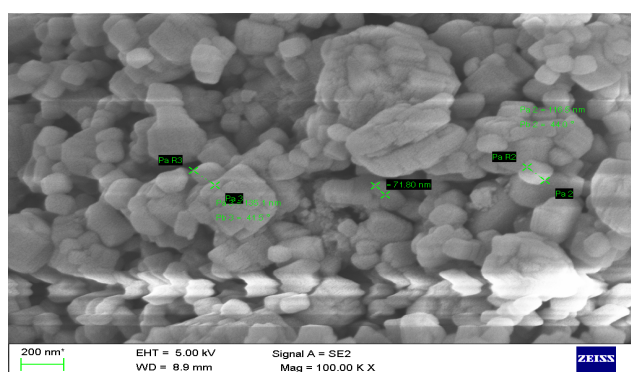


Figure 12. Morphology of $(K_{0.48}Na_{0.52})NbO_3$

Further 800°C curves ensure increase in the crystallite size from 9.796 \pm 0.52 nm to 11.242 \pm 0.71 nm at 10h linearly, indicating further growth is essential. Thereafter, 900°C curve initiated crystallite size from 14.402 \pm 0.73nm to almost consistent value across 7h (16.112 nm) and an reduction in the crystallite size at 10h (15.112 nm \pm 0.79 nm) indicating linear complete

grain growth of calcined powder and completion of solid state chemical reaction.

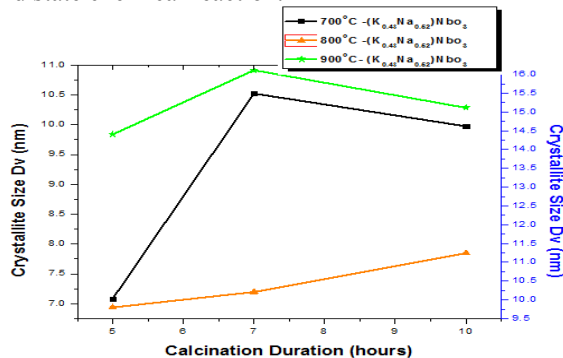


Figure 13. Crystallite size of calcined (K_{0.48}Na_{0.52})NbO₃ powders at 700, 800 and 900°C for different.

3.6. Energy Dispersion spectroscopy of calcined KNN powder

The formation of complex oxides at 900°C, 10h calcined nano-powders was observed by X-ray diffraction results. This was attributed to energy dispersion spectroscopy study of calcined KNN powders as shown in Figure 14a., Figure 14b. and Figure 14c. The EDS microanalysis at 900°C, 10h Figure 14c. representing KNN calcined powder shows elevated level of K, Nb, and Oxygen elements resulting in the formation of complex oxides. This indicates low reactivity when compared to Figure 14a. and Figure 14b. which is representing the normal composition of the KNN particles. The existence of K⁵⁺ rich particles results in the formation of stoichiometric compositional discrepancy in KNN nano-powders.

Carbon element and its edge energy which were seen at 700 °C [TABLE 8] and 800°C [TABLE 9] spectrum having cross-section of 10µm and 20µm was however not visible in EDS of 900°C spectrum of 20µm cross section [TABLE 10]. This is due to the decomposition of carbonates into bicarbonate and it was associated with 800°C and 900 °C, 10h EDS spectrum [TABLE 8, 9]. This decomposition was initiated by the reduction of carbon element in its wt% by 2.27 and atomic % by 2.81 attributing to 800°C, 10h EDS data [TABLE 9]. The absence of carbon element in EDS results at 900°C, 10h ensured that solid state chemical reaction is completed with the formation of the require system (K_{0.48}Na_{0.52})NbO₃ [TABLE 10]. But 900°C, 10h EDS also reveals increased percentage of K (wt % by 0.2, at% by 1.04), Nb (wt % by 8.28, at% by 39.99) and oxygen (wt% by 1, at% by 10.65) elements which is the reason behind the formation of complex oxides. These results are in agreement with X-ray diffraction data of KNN calcined powders. The elemental table of 900°C, 10h EDS spectrum [TABLE 10] for KNN calcined powder is associated with elemental oxygen by 28.01 wt % and 62.71 at% along with the edge energy of 0.537 (keV).

The weight and atomic percentage of Sodium was 4.62 wt% and 7.19 at% followed by the edge energy and edge jump of 1.072 (keV) and 11.71, respectively. In the case of Potassium, it was 7.77 wt% and 7.12 at% with the edge energy and edge jump of 3.60 (keV) and 8.8368, respectively. Finally, niobium consisted of 59.61wt% and 22.98 at% with edge energy of L (2.69ke V) followed by the edge jumps of 1.15 indicating a strong potential for piezoelectric charge constant.

TABLE 8. The SEM-EDS of [(k_{0.48} Na_{0.52})] NbO₃ powders calcined at 700°C for 10h taken at a scan of 10µm.

Element	Weight%	Atomic%
C K	7.42	16.01
O K	27.01	52.06
Na K	6.67	9.10
K K	7.57	6.08
Nb L	51.33	17.01
Totals	100.00	

TABLE 9. The SEM-EDS of [(k_{0.48} Na_{0.52})] NbO₃ powders calcined at 800°C for 10h taken at a scan of 20µm.

Element	Weight%	Atomic%
C K	5.15	13.20
O K	26.26	51.69
Na K	5.97	8.58
K K	8.72	7.36
Nb L	53.90	19.17
Totals	100.00	

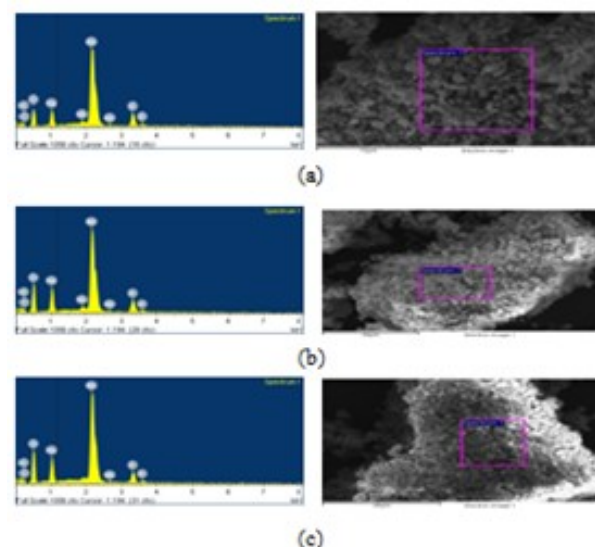


Figure 14. EDS Spectrum of (a) 700°C (b) 800°C (c) 900°C of 10h calcined (k_{0.48}Na_{0.52})NbO₃ nano-powders.

3.7 Microwave Sintering and characterization of sintered KNN ceramics

The green samples

were densified by using microwave sintering at 1080°C for 30 min. The relative density of the sintered samples was determined by Archimedes principle using densitometer. The physical properties of microwave-sintered KNN ceramics are mentioned in TABLE 12. The SEM images of $(K_{0.48}Na_{0.52})NbO_3$ ceramics, microwave-sintered at 1080°C at a scan of 10µm, 1µm, and 200nm is shown in Figure 15. Here dense and uniform microstructure was visible with reduced particle size in range of 75.81 nm-100.8 nm when compared with morphology of calcined KNN nano-powders. The X-ray diffraction data of the sintered KNN ceramics at 1080°C for 30min is shown in Figure 16. The result depicts complete growth of the perovskite structure across the plane (001), (101) for 2θ value in the range of 20-35° with full intensity.

The peak split up was visible from 45-60° which showed the presence of phase transformation from orthorhombic to tetragonal without the formation of secondary phases. The required transformation was associated with (200), (102) and (111) planes. The lattice parameters of sintered KNN ceramics is shown in TABLE 11. which ensure tetragonal structure being dominant one as almost all the lattice parameter for 2θ values satisfied ($a = b \neq c$) and ($\alpha = \beta = \gamma$).

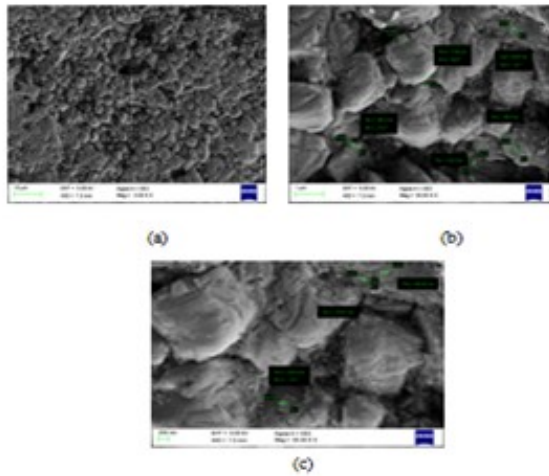


Figure 15. Morphology $(K_{0.48}Na_{0.52})NbO_3$ (a) 10µm, (b) 1µm, (c) 200µm, Microwave sintered ceramics at 1080°C.

TABLE 10. The SEM-EDS of $[(k_{0.48}Na_{0.52})]NbO_3$ powders calcined at 900°C for 10h taken at a scan of 20µm.

Element	Weight%	Atomic%
C K	0.00	0.00
O K	28.01	62.71
Na K	4.62	7.19
K K	7.77	7.12
Nb L	59.61	22.98
Totals	100.00	

The dielectric constants (ϵ_r) of $(K_{0.48}Na_{0.52})NbO_3$ ceramics at 1kHz, 10kHz, 100kHz, 1MHz, 1.1MHz and 1.3MHz for high temperature measurements from 20°C -200°C are shown in Figure 17. The dielectric constant of sintered KNN at 1080°C gradually increased from 1kHz to 1.3MHz. The maximum value of dielectric constant achieved was 2782.22 for 1.3 MHz at 200°C.

TABLE 11. Unit cell parameters of sintered $(K_{0.48}Na_{0.52})NbO_3$ ceramics at 1080°C for 30 min.

No.	a [Å]	b [Å]	c [Å]	Alpha [°]	Beta [°]	Gamma [°]	Cell Volume [Å ³]	Indexing M...	Not index.	POM
2	5.5833	5.5833	4.0007	90.0000	90.0000	90.0000	124.7140	Treor	2	40.0000
3	3.9480	3.9480	8.0014	90.0000	90.0000	90.0000	124.7140	Treor	2	37.0000
4	3.9480	3.9480	12.0021	90.0000	90.0000	90.0000	187.0709	Treor	2	26.0000
5	7.8960	7.8960	4.0007	90.0000	90.0000	90.0000	249.4281	Treor	2	22.0000
6	7.8966	7.8966	4.9297	90.0000	90.0000	120.0000	266.2179	Treor	3	33.0000
7	5.6721	5.6721	20.7408	90.0000	90.0000	120.0000	577.8797	Treor	3	77.0000
8	11.3892	11.3892	5.6169	90.0000	90.0000	120.0000	630.9720	Treor	2	23.0000
9	11.2405	11.2405	5.9205	90.0000	90.0000	120.0000	647.8316	Treor	3	31.0000
14	8.0075	8.0075	9.0057	90.0000	90.0000	90.0000	577.4449	Treor	0	11.0000
10	5.6660	5.6437	3.9465	90.0000	90.0000	90.0000	126.1980	Treor	0	32.0000
11	5.6592	5.6592	3.9467	90.0000	90.0000	90.0000	126.3982	Treor	2	50.0000
12	5.6592	5.6592	3.9467	90.0000	90.0000	90.0000	126.3982	Treor	2	50.0000
13	8.0079	8.0079	9.0052	90.0000	90.0000	90.0000	577.4730	Treor	0	12.0000
15	8.0075	8.0075	9.0057	90.0000	90.0000	90.0000	577.4449	Treor	0	11.0000
1	3.9480	3.9480	4.0007	90.0000	90.0000	90.0000	62.3570	Treor	2	72.0000

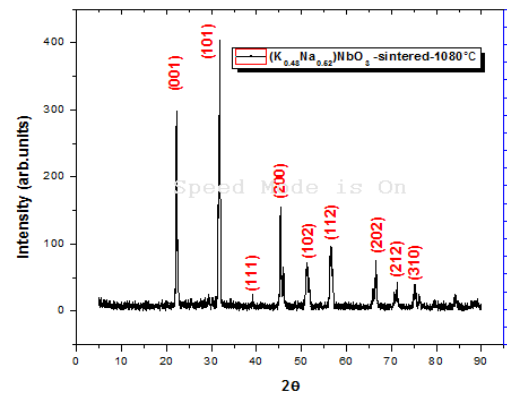


Figure 16. XRD patterns of sintered

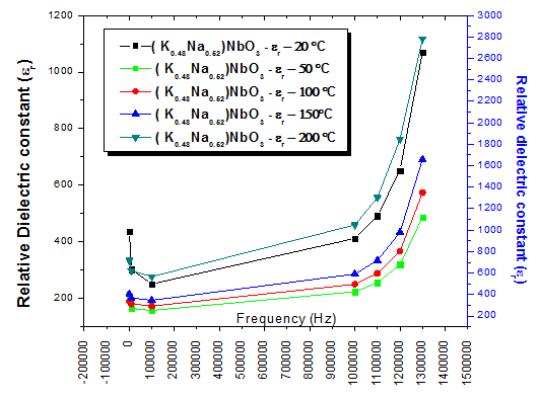


Figure 17. Relative dielectric constants of sintered $(K_{0.48}Na_{0.52})NbO_3$ ceramics at 1080°C.

The dielectric losses ($\tan\delta$) of $(K_{0.48}Na_{0.52})NbO_3$ ceramics at 1kHz, 10kHz, 100kHz, 1MHz for high temperature measurements ranging from 20°C to 200°C are shown in Figure 18. The dielectric losses for $(K_{0.48}Na_{0.52})NbO_3$ ceramics at 1080°C was 0.5087 at 1kHz for 20°C and reduced to 0.1292 at 1MHz. But as the temperature was increased, the losses were lower comparatively till 100 kHz and increased slightly at 1MHz ensuring that high temperature electrical measurements helped in reducing dielectric losses. The piezoelectric charge constant (d_{33}) of poled samples at 3kV/mm in silicon oil bath at 30°C, 100°C, 175°C and 185°C is shown in Figure 19. The d_{33} value at room temperature was the least and the piezo-electric charge constant increased gradually and reached the maximum value of 154pC/N. This ensured that d_{33} value will be the maximum near the metaphoric phase boundary [MPB] of KNN. The summary of physical and electrical properties (high temperature measurements) of sintered KNN ceramics at different frequencies are shown in TABLE 12 and TABLE 13. The maximum electromechanical coupling coefficient (K_p) was found to be 0.5394 at 100°C, mechanical quality factor of 900.25 and frequency constant N_p of 12900 (Hz.m) at 50°C, highest d_{33} value of 125pC/N poled at 185°C with least dielectric loss of 0.02362 at 1kHz at 50°C.

TABLE 12. Summary of physical and electrical properties of microwave sintered $(K_{0.48}Na_{0.52})$ at 1080°C, 30min.

Sintering Process	Density (g/cm ³)	Relative density	Mean crystallite size(nm)	Frequency	ϵ_r at 20°C	ϵ_r at 50°C	ϵ_r at 100°C	ϵ_r at 150°C	ϵ_r at 200°C
Microwave	4.2953	95.23	11.59	1kHz	436	364	338	406	717
				10kHz	302	270	313	369	619.65
				100kHz	251	252	292	346	566.37
				1MHz	412	426	495	591	1048.26
				1.1MHz	492	509	596	717	1302.42
				1.2MHz	652	679	803	979	1846.54
1.3MHz	1070	1120	1350	1660	2782.22				

TABLE 13. Summary of electrical and mechanical properties of microwave sintered $(K_{0.48}Na_{0.52})$ at 1080°C, 30min.

Frequency for Dielectric losses	$\tan\delta$ 20°C	$\tan\delta$ 50°C	$\tan\delta$ 100°C	$\tan\delta$ 150°C	$\tan\delta$ 200°C	Poling Temp at 110Hz	d_{33} (pC/N)	Electrical measurement temperature	K_p	Q_m	N_p (Hz.m)
1kHz	0.50872	0.02362	0.06131	0.07784	0.09126	30	48	20	0.17025	283.13	12800
10kHz	0.33712	0.02485	0.05124	0.03541	0.08173	100	80	50	0.47628	900.25	12900
100kHz	0.14485	0.03348	0.04573	0.04797	0.05897	170	125	100	0.53944	819.93	12600
1MHz	0.12926	0.10506	0.10283	0.11877	0.17143	185	154	150	0.50854	744.25	12800
								200	0.4791	57.28	12800

4. CONCLUSION

The following conclusions were observed during the course of this study.

1. KNN piezoelectric ceramics in the system of $(K_{0.48}Na_{0.52})NbO_3$ was synthesized successfully by optimizing ball milling parameters to achieve homogenous powder.

2. Analysis of calcination parameters on blended KNN powders helped in establishing optimized calcination temperature (900°C,7h) for completion of solid state chemical reaction and to synthesize $(K_{0.48}Na_{0.52}) NbO_3$ nano-powders without formation of secondary phases which was in agreement with diffraction and energy dispersion spectroscopy results.
3. The cubic crystal structure with good compactness revealed by the morphology study at 900°C, 7h calcined $(K_{0.48}Na_{0.52}) NbO_3$ powder was in good agreement with the diffraction and transmittance results of 900°C, 7h KNN powders in which perovskite structure was the dominant one.
4. X-ray diffraction results of calcined $(K_{0.48}Na_{0.52}) NbO_3$ powder and its lattice parameters ensured the formation of phase transformation and tetragonal structure being the dominant one at 900°C, 10h.
5. The estimated crystallite size using X-ray diffraction data was in the required grain size range between 7.08nm (700°C) and 16.11 nm (900°C) due to the optimization of the synthesis and calcination processes.
6. Morphology study revealed that particle size of calcined KNN powders was in the range of 65nm-135nm with uniform grain growth, which is one of the densification properties to achieve good piezoelectric charge coefficient in $(K_{0.48}Na_{0.52}) NbO_3$.
7. Optimized calcination and microwave sintering of KNN ceramics helped in achieving relative density of 95.23%, with optimum dielectric and piezoelectric properties of $\epsilon_r = 2782.22$, $d_{33} = 125pC/N$, $\tan\delta = 0.05897$, $N_p = 12800$, $K_p = 0.54$, $Q_m = 900.25$ for pure KNN microwave-sintered at 1080°C for 30min.

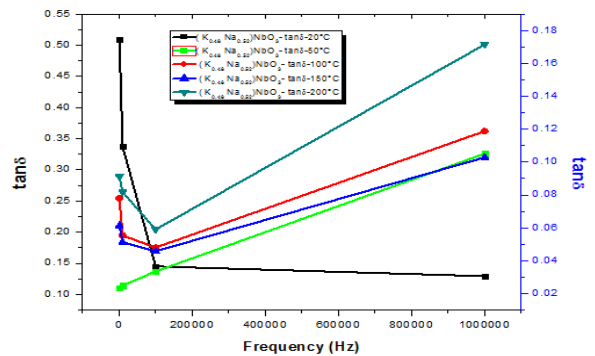


Figure 18. Dielectric Loss of sintered

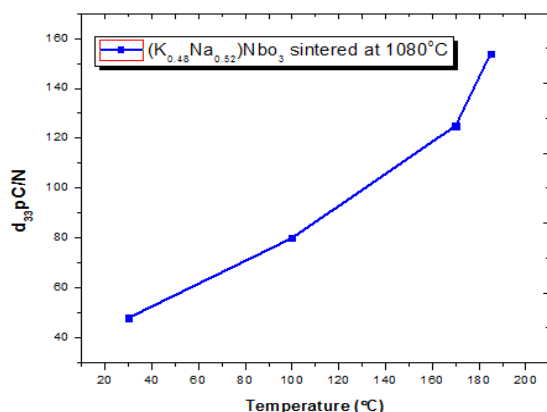


Figure 19. Piezo-electric charge constant of sintered

5. ACKNOWLEDGMENTS

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