

SYNTHESIS AND CHARACTERIZATION OF LEAD-FREE PIEZOELECTRIC $(K_{0.5}Na_{0.5})NbO_3$ PRODUCED WITH IMPROVED CALCINATION TEMPERATURE

Nor Amalina Ahmad^{a*}, Dzetty Soraya Abdul Aziz^a, Norni Hidayawati Mat Daud^a, Rahim Noor^b, Amir Azam Khan^b

^aCentre for Pre-University Study, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

^bFaculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia

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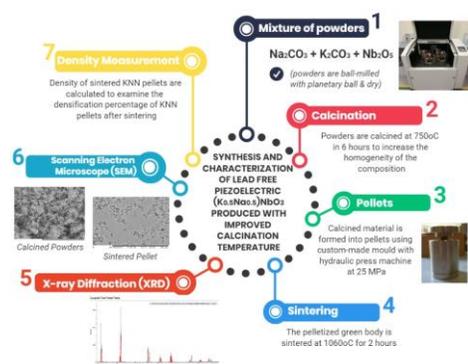
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*Corresponding author
anamalina@unimas.my

Graphical abstract



Abstract

Potassium sodium niobate (KNN) is one of the lead free piezoelectric material that catch the attention of researchers and also those in the industrial field because of its stable piezoelectric responses and environmental friendly composition. The recent development of KNN shows that many methods have been used to synthesize the KNN but the stoichiometric $Ka_{0.5}Na_{0.5}NbO_3$ composition is extremely difficult to consolidate. One of the ways to overcome the problem is to precisely pre-calcine and use milling process for proper homogenization followed by natural sintering process. In this paper, attempt has been made to synthesize the KNN produced at 750 °C calcination temperature. The results of 1060°C sintering temperature for 2 hours show a good composition of KNN with orthorhombic crystal structure where the final sintered pellet can reach to a relative density up to 87.13 %.

Keywords: Lead-free piezoelectric, KNN, perovskites, sintering, microstructure

Abstrak

Kalium Natrium Niobat (KNN) merupakan salah satu bahan piezoelektrik bebas plumbum yang mendapat perhatian penyelidik dan bidang industri disebabkan oleh tindak balas piezoelektrik yang stabil dan komposisinya yang mesra alam. Perkembangan KNN terkini menunjukkan pelbagai kaedah dapat dilakukan untuk menghasilkan KNN namun komposisi stoikiometri $Ka_{0.5}Na_{0.5}NbO_3$ sangat sukar diperolehi. Salah satu kaedah untuk mengatasi masalah ini adalah dengan pra-pemanasan dan menggunakan proses pengisaran bagi mendapatkan homogenisasi yang seimbang diikuti proses persinteran secara semulajadi. Dalam kajian ini, percubaan bagi menghasilkan KNN telah dijalankan pada suhu pemanasan 750 °C. Hasil persinteran pada suhu 1060 °C selama 2 jam menunjukkan komposisi KNN terbaik dengan struktur kristal ortorombik di mana pelet tersebut telah mencapai ketumpatan relatif setinggi 87.13 %.

Kata kunci: Piezoelektrik bebas plumbum, KNN, perovskit, persinteran, mikrostruktur

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1.0 INTRODUCTION

Piezoelectric materials based on lead perovskite such as lead zirconium titanate (PZT) and sodium bismuth titanate (NBT) have been widely used for their piezoelectric and ferroelectric properties. The applications of piezoelectric materials include transducers, the devices which convert electrical energy into mechanical strain or vice versa, phonograph cartridges, microphones, speakers, audible alarms, and ultrasonic imaging [1].

Bhalla *et al.* (2017) describes that PZT ceramics are stiff and brittle variant which are used in many applications such as accelerometers, strain sensors, stress wave emitters and receivers, actuators, vibration sensors and pressure transducers [2, 3]. However, the usage of lead-based piezoelectric ceramics is slowly being expelled from the industry owing to concerns regarding their toxicity as they contain more than 60% weight percentage of lead [4, 5]. Moreover, Aksel and Jones (2010) add that the lead-based materials are not environmentally friendly due to high lead emission to the air during the materials synthesis [6, 7, 8]. The fact that the excessive lead release will cause harm to environment is also supported by Dahiyaa and Takura (2014) saying that the environmental issues and cases regarding human health caused by constant inhalation of lead particles were frequently associated with the common use of PZT based materials containing almost 60% weight percentage of lead which being released through lead evaporation to the air during the sintering process [9].

Based on the concerns of lead negative effects on the environment and health, research has been conducted to produce the lead-free based piezoelectric ceramics. Among numerous examples are piezoelectric materials based on alkaline niobate ($\text{Na}_{0.5} \text{K}_{0.5} \text{NbO}_3$ abbreviated as KNN, which show the most promising results due to their relatively acceptable piezoelectric as well as ferroelectric properties and being compatible with the environment [10]. Ohbayashi and other researchers also characterized the alkali niobate KNN which exhibits fairly good piezoelectric characteristics and high Curie temperature [11-16].

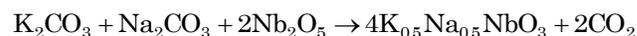
The major problem related to alkaline niobate is during the synthesis and sintering process. According to the Barbara Malic *et al.* (2008), the stoichiometric ($\text{Na}_{0.5} \text{K}_{0.5} \text{NbO}_3$) is extremely difficult to consolidate [17, 18]. If the KNN can be properly synthesized and problems regarding obtaining the fine samples are resolved, the material will be useful in many applications such as ultrasonic motors, actuators, inkjet heads and transducers [11]. Ohbayashi (2016) also states that one of the ways to overcome the problems is by hot-press sintering method which is reported to further decrease the crystal grain size, increase the density of the ceramics from 4.25 to 4.46 g/cm³, and doubles the piezoelectric constant d_{33} from 80 to 160 pC/N [11]. The claim also being

supported by Birol *et al.* (2005) by stating that the hot pressing can be an alternative solution to produced fine high densified samples [19]. Birol *et al.* (2005) again added that, although this method yields high densities and better properties compared to air sintered method, it still needs to carefully investigate and the sintering parameters need to be optimized to result in reproducible and high-quality ceramics [19].

Therefore, in the present work, potassium sodium niobate (KNN) has been synthesized at different temperatures following a reactive sintering process. The microstructural properties of KNN at calcination and sintering stage have been investigated and discussed in detail.

2.0 METHODOLOGY

$\text{K}_{0.5} \text{Na}_{0.5} \text{NbO}_3$ powders were synthesized by a conventional solid state reaction method [20, 21]. 0.308 g Sodium carbonate (Na_2CO_3 , 99 % purity, Merck), 0.401 g potassium carbonate (K_2CO_3 , 99 % purity, Merck) and 1.54 g niobium oxide (Nb_2O_5 , 99% purity, Sigma Aldrich, USA) were used as starting precursors. Initially, these three powders were dried separately in an oven at 200 °C for 2 hours [22] and then were weighed for each composition according to a stoichiometric formula as given by:



The powders were instantly put into a 50 ml tungsten carbide jar that was initially filled with 40 ml acetone. Retsch PM100 planetary ball mill was used with 25 number of tungsten balls for mixing and wet milling within 3 hours at speed of 300 rpm. The slurry formed after wet milling was sieved and dried in convection oven at 120 °C for 2 hours to remove the acetone solution. The dried slurry was dry milled once again for 30 minutes to break down the hard agglomerates formed from the previous milling process. The powders were re-dried again at 120 °C for 1 hours in order to remove some moisture that was absorbed by the powders during previous milling process since the powders easily absorb moisture.

According to Mahesh and Pamu (2015), the best calcined temperature is 700 °C due to the highest dielectric constant and lower dielectric loss [26]. To increase the homogeneity of the composition, the calcination process in this research was carried out for temperature 650 °C and 750 °C. Both calcinations were carried out for 2 hours and 6 hours respectively in order to determine the best calcination temperature for the earliest formation of KNN compositions. The XRD spectra were obtained using Bruker D8 Advance after calcination of samples to determine the presence of earliest KNN phase as well as choosing the best samples of KNN formation for sintering process. The optimized sample was further analyzed using Hitachi (TM3030) SEM to observe the

grain's microstructure [23]. The calcined material was formed into pellets using a custom-made mould and cold pressed with hydraulic press machine at 25 MPa. The pelletized green body of the chosen samples was sintered for 2 hours at different temperatures of 1060 °C and 1100 °C by using the heating rate of 5 °C/min.

3.0 RESULTS AND DISCUSSION

3.1 X-ray Diffraction (XRD) of Calcined KNN Powders

The calcination was carried out at 650 °C and 750 °C for 2 hours and 6 hours for each temperature. Figures 1(a) and 1(b) show the XRD patterns of the KNN ceramics calcined at 650 °C for 2 hours and 6 hours, respectively. The Figures 2(a) and 2(b) show the XRD patterns of the KNN ceramics calcined at 750 °C for 2 hours and 6 hours, respectively.

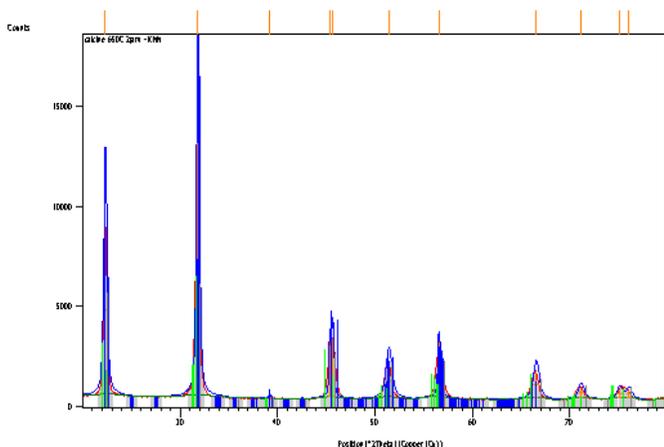


Figure 1(a) XRD result of calcined KNN powders at 650 °C for 2 hours

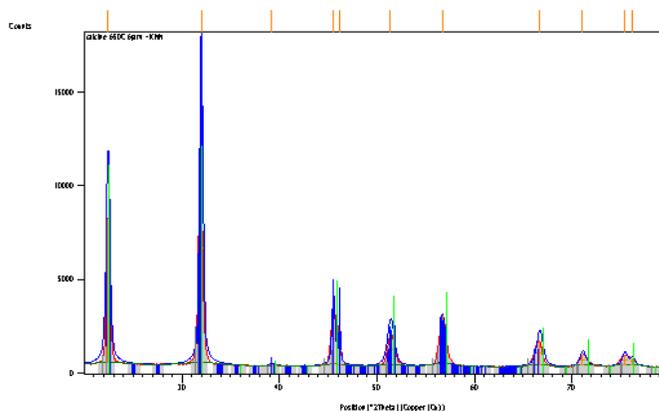


Figure 1(b) XRD result of calcined KNN powders at 650 °C for 6 hours

The KNN peaks can be observed from Figure 1(a) and 1(b) which is indicated by the KNN peak angles. Through comparison between the measured to the data peaks, it can be seen that the area under the peaks are broadened which reduced the sharpness of the graph. The broadened area represent the small size of grains with lower crystallinity, thus lead to the incomplete reaction. Noises can be seen from the graphs which represent the incomplete crystallization of the particles. As we know the good crystallinity will provide the better function of piezoelectric material.

The different colors in XRD pattern show the existence of other phases of KNN compound with different ratio and also non-KNN compounds. Table 1 shows the percentage of each compound existed after the calcination process. The existence of these multiphase of KNN is due to the incomplete reaction of the particles which probably was caused by the insufficient temperature.

Table 1 Table of multiphase pattern for calcined KNN at 650 °C within 2 hours and 6 hours

Duration	Peak's Color	Compounds Name	Chemical Formula	Score of matched peaks count (%)	Lattice Structure
2 hrs	Blue	Potassium Sodium Niobate	$(K_{0.65}Na_{0.35})NbO_3$	72	Monoclinic
	Green	Potassium Niobate	$KNbO_3$	28	Orthorhombic
	Grey	Sodium Niobate	$NaNbO_3$	42	Tetragonal
6 hrs	Blue	Potassium Sodium Niobate	$(K_{0.65}Na_{0.35})NbO_3$	79	Monoclinic
	Green	Potassium Sodium Niobate	$(K_{0.1}Na_{0.9})NbO_3$	52	Tetragonal
	Grey	Potassium Niobate	$KNbO_3$	24	Tetragonal

From Table 1, it can be seen that the highest % matching in peaks is Potassium Sodium Niobate $(K_{0.65}Na_{0.35})NbO_3$ with percentage 72% for 2 hours sample and 79% for 6 hours sample. The crystal structure for this sample was obtained from XRD analysis. It shows that $(K_{0.65}Na_{0.35})NbO_3$ for both durations is exist as monoclinic lattice structure. For 6 hours sample, the other phase of KNN compound with chemical formula of $(K_{0.1}Na_{0.9})NbO_3$ is detected with percentage of 52% and existed as tetragonal

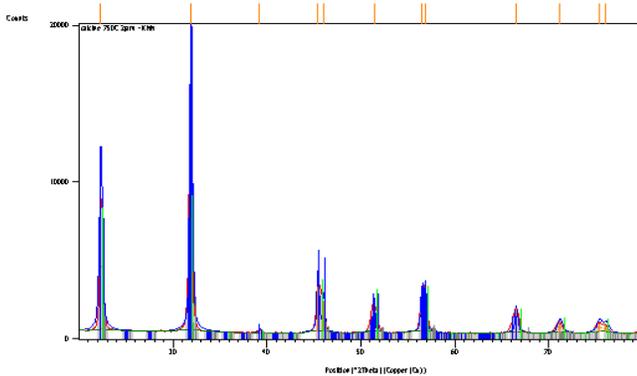


Figure 2(a) XRD result of calcined KNN powders at 750 °C for 2 hours

lattice structure. The non-KNN phases such as Potassium Niobate and Sodium Niobate exhibit least scores.

Figures 2(a) and 2(b) show the XRD patterns of the KNN ceramics calcined at 750 °C for 2 hours and 6 hours, respectively. The KNN phase can be observed from the graph which is indicated by the KNN peak angles in Table 2.

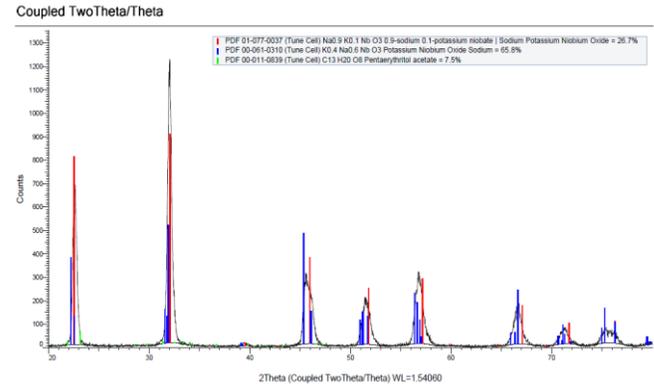


Figure 2(b) XRD result of calcined KNN powders at 750 °C for 6 hours

Table 2 Table of multiphase pattern for calcined KNN at 750 °C within 2 hours and 6 hours

Duration	Peak's Color	Compounds Name	Chemical Formula	Score of matched peaks count (%)	Lattice Structure
2 hrs	Blue	Potassium Sodium Niobate	$(K_{0.65}Na_{0.35})NbO_3$	80	Monoclinic
	Green	Potassium Sodium Niobate	$(K_{0.1}Na_{0.9})NbO_3$	41	Tetragonal
	Grey	Sodium Niobate	$NaNbO_3$	16	Orthorhombic
6 hrs	Blue	Potassium Sodium Niobate	$(K_{0.65}Na_{0.35})NbO_3$	65.8	Monoclinic
	Red	Potassium Sodium Niobate	$(K_{0.1}Na_{0.9})NbO_3$	26.7	Tetragonal

Table 2 shows that sample calcined at 750 °C, exhibits the highest % Potassium Sodium Niobate $(K_{0.65}Na_{0.35})NbO_3$ with percentage 80%. The longer calcination time is not suitable in this case, since the samples are not compressed but in loose powder form hence open to attack by the atmosphere. It would be interesting to see the same results conducted in inert atmosphere This $(K_{0.65}Na_{0.35})NbO_3$ shows monoclinic lattice structure.

For both samples, the other phase of KNN compound with chemical formula of $(K_{0.1}Na_{0.9})NbO_3$ is detected with 41% and 26.7% peak matching as tetragonal lattice structure. The non-KNN phase such as Sodium Niobate is appeared with the least scores. This indicates that the acetone molecule is not fully removed from the powders after the calcination

process. However, the trace of acetone can be removed during the annealing process during sintering later.

The compound of $(K_{0.65}Na_{0.35})NbO_3$ obtained from all samples has a chemical composition near to the ideal $(K_{0.50}Na_{0.50})NbO_3$. Therefore, the sample that possessed the most score of this compound is the sample calcined at 750 °C for 2 hours. Hence, for the next step which is sintering process, 750 °C samples for 2 hours and 6 hours duration are chosen.

3.2 X-ray Diffraction (XRD) of Sintered KNN Pellets

The chosen calcined powders were cold pressed into pellets and sintered for 2 hours at two different temperatures (1060 °C and 1100 °C). Figures 3(a) and 3(b) show the XRD patterns of sintered KNN pellets at 1060 °C which have been calcined at 750 °C within 2 hours and 6 hours, respectively. While, Figures 4(a) and 4(b) show the XRD patterns of KNN pellets sintered at 1100 °C which have been calcined at 750 °C for 2 hours and 6 hours, respectively.

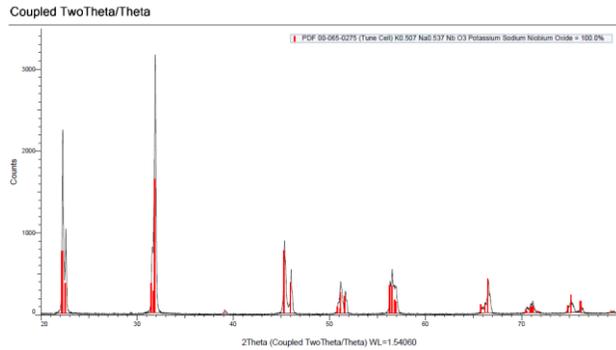


Figure 3(a) XRD result of KNN pellets sintered at 1060 °C, calcined at 750 °C for 2 hours

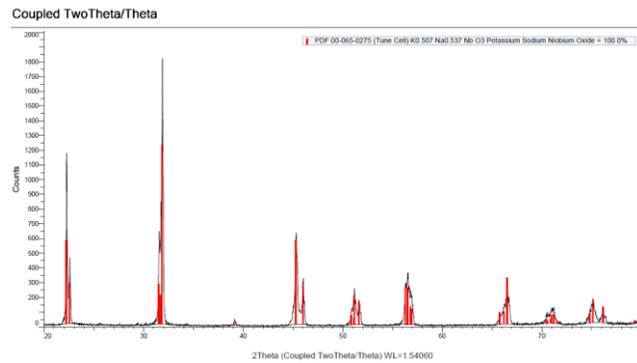


Figure 3(b) XRD result of KNN pellets sintered at 1060 °C, calcined at 750 °C for 6 hours

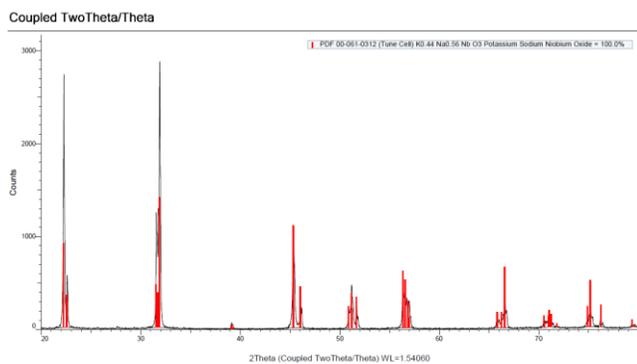


Figure 4(a) XRD result of KNN pellets sintered at 1100 °C, calcined at 750 °C for 2 hours

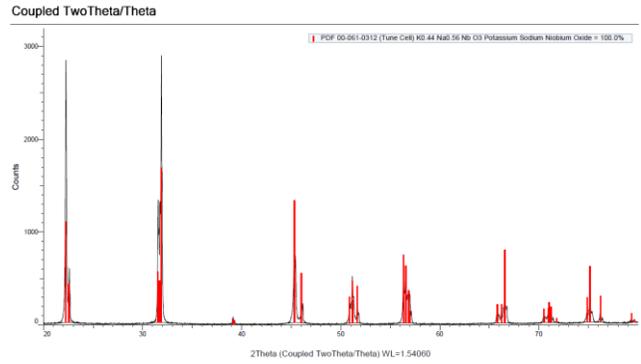


Figure 4(b) XRD result of KNN pellets sintered at 1100 °C, calcined at 750 °C for 6 hours

As observed from Figures 3(a) – 4(b), the XRD pattern for all samples show sharp peaks and show less area under the curve compared to the calcined XRD patterns. The area under the curve for 1100 °C sintered sample is less compare to the 1060 °C sintered sample. For both 1100 °C sintered samples, the peaks are sharper and reached higher intensity value. The sharpness of the peaks is a good indicator on the formation of crystallinity in the samples.

Table 3 Multi-Phase pattern for sintered KNN pellets

Calcination time at 750°C (hours)	Sintering Temperature (°C) for 2 hours	Chemical Formulae	Lattice Structure
2	1060	(K _{0.507} Na _{0.537}) NbO ₃	Orthorhombic
	1100	(K _{0.44} Na _{0.56}) NbO ₃	Monoclinic
6	1060	(K _{0.507} Na _{0.537}) NbO ₃	Orthorhombic
	1100	(K _{0.44} Na _{0.56}) NbO ₃	Monoclinic

Table 3 provides evidence that there is no existence of non-KNN phase for all sintered samples. Based on the results, samples that have been sintered for 1060 °C had chemical formula of (K_{0.507}Na_{0.537}) NbO₃ and gives an orthorhombic lattice structure while the samples which have been sintered at 1100 °C had a monoclinic lattice structure. Based on the previous research, the ideal KNN has a chemical composition of (K_{0.5}Na_{0.5}) NbO₃ and possess an orthorhombic lattice structure at room temperature (Yang *et al.*, 2018). In crystallography, monoclinic and orthorhombic crystal structures belong to the same system where the orthorhombic has 3 mutually orthogonal axes while the monoclinic has only 2 axes that are perpendicular to each other. Therefore, resulting peaks very slightly shift in angle in XRD analysis. Based on the XRD results in Figure 3(a) and Figure 4(a), there are no new peaks which appeared,

but the angle of reflection are very slightly shifted which represent two different crystal structures; orthorhombic and monoclinic. In this case, the samples sintered at 1060 °C have the closest structure with the ideal KNN piezoelectric material which possess similar orthorhombic lattice structure and the chemical composition is near $(K_{0.5}Na_{0.5})NbO_3$.

3.3 Density Measurement for Sintered KNN Pellets

The densities of sintered KNN pellets were calculated by measuring the height and the diameter of the

pellet by using caliper. While the mass of the pellets was measured using an electronic beam balance. The percentage of densification can be determined by calculating the density of the pellets, before and after sintering which is tabulated as shown in Table 4.

From the observation, the densification is better at higher sintering temperature (1100 °C). This is due to the faster diffusion processes which homogenized the microstructure [24-25].

Table 4 Table of densification percentage for sintered KNN pellets

Calcination at 750 °C duration (hours)	Sintering parameters	Density before sintering ($g \cdot mm^{-2}$)	Density after sintering ($g \cdot mm^{-2}$)	Percentage of densification (during sintering, from green body to sintered body) (%)	Percentage of densification (ratio measured/theoretical density) (%)
2	1060 °C for 2 hours	1.845×10^{-3}	3.842×10^{-3}	51.98	85.00
6		1.883×10^{-3}	3.930×10^{-3}	52.09	87.13
2	1100 °C for 2 hours	1.854×10^{-3}	3.945×10^{-3}	53.00	87.47
6		1.865×10^{-3}	3.777×10^{-3}	50.53	83.51

3.4 Scanning Electron Microscopy (SEM)

The images shown in Figures 5(a) and 5(b) indicate that the starting powders have still not completely reacted with each other. There are spaces between grain clusters which is a sign that the grains have already reacted to each other but at the same time there are still many spaces between the clusters and grains which indicate unreacted KNN grains. On the average, the grain size of the calcined powders is consisting of nano-sized particle which indicates that the particle has a potential to further react with each other which can only be achieved through sintering.

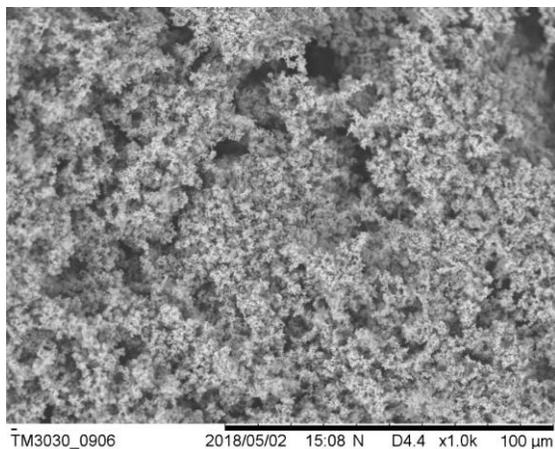


Figure 5(a) Calcined KNN Powders at 750 °C for 2 hours

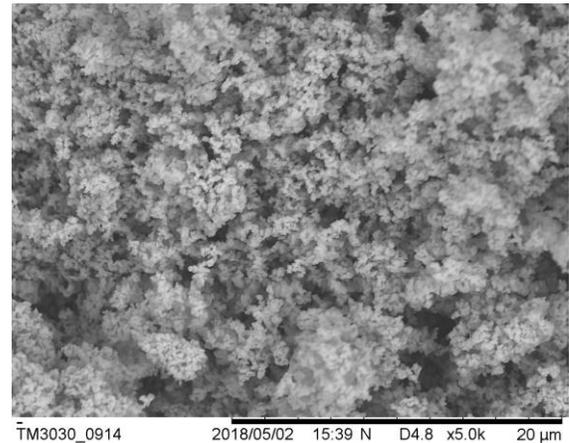


Figure 5(b) Calcined KNN Powders at 750 °C for 6 hours

The SEM images that were taken after the sintering show that most of the grains were reacted with each other during the sintering process. The trace of after necking could be observed by noticing the slightly dark area at the smooth surfaces. From the images, it can also be observed that the growth of the grains and densification occurs in most cases, except a few places where porosity can be observed (Figures 6(a) to (d)). For the samples being sintered at 1060 °C, the results can be observed in Figure 6(a) for samples calcined for 2 hours and Figure 6(b) for samples calcined at 6 hours.

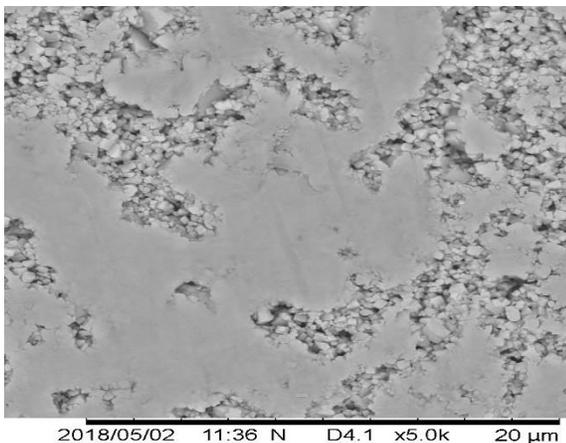


Figure 6(a)(i) KNN pellets sintered at 1060°C and been calcined at 750°C for 2 hours (x5000)

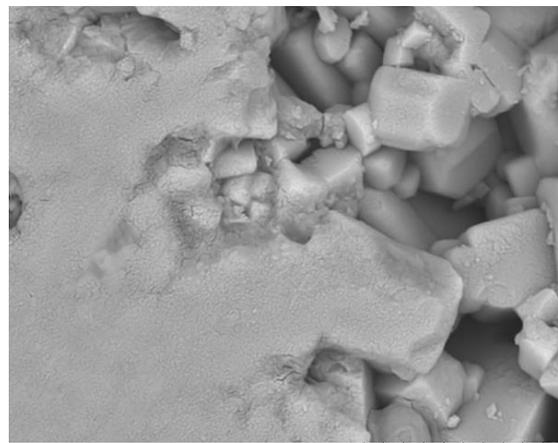


Figure 6(c)(ii) KNN pellets sintered at 1100 °C and been calcined at 750°C for 2 hours (x12000)

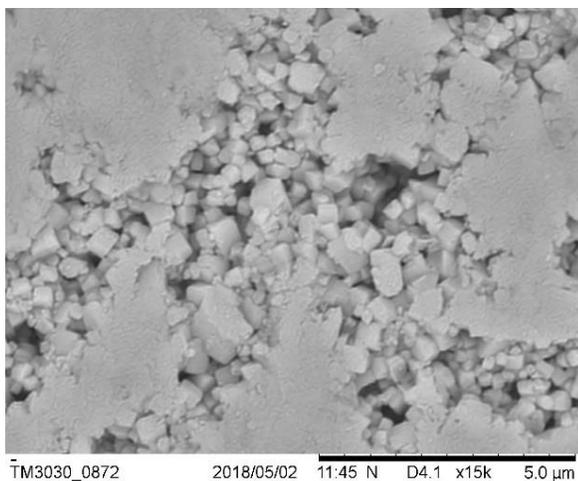


Figure 6(b)(ii) KNN pellets sintered at 1060 °C and been calcined at 750°C for 6 hours (x10000)

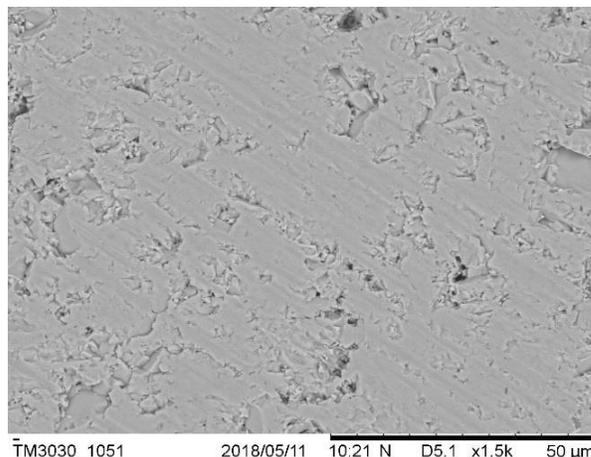


Figure 6(d)(i) KNN pellets sintered at 1100 °C and been calcined at 750 °C for 6 hours (x1500)

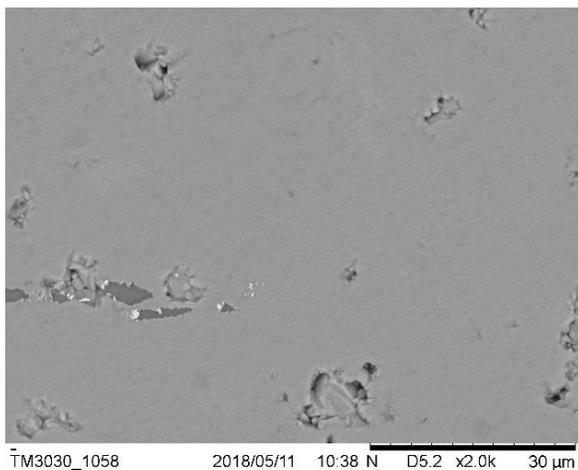


Figure 6(c)(i) KNN pellets sintered at 1100 °C and been calcined at 750 °C for 2 hours (x2000)

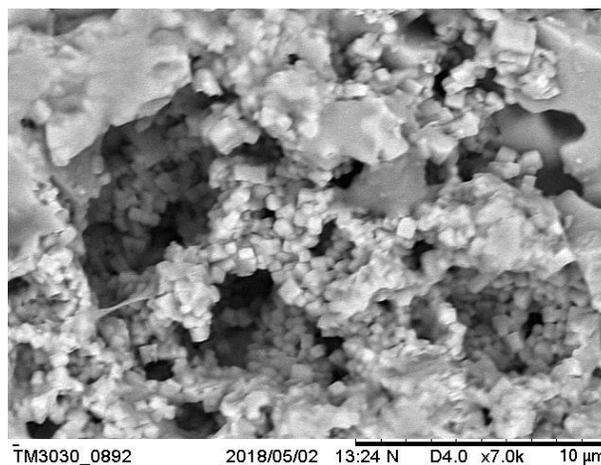


Figure 6(d)(ii) KNN pellets sintered at 1100°C and been calcined at 750°C for 6 hours (x7000)

In Figure 6(a), the signs of the grains reacted and fused with each other could be seen for most of the area in the figure, however there still remains some regions which are not completely sintered with the neighbouring grains. It can be assumed that the main cause is incomplete compaction during cold pressing, which prevents the grains to react with each other.

Besides the calcination time, the sintering temperature is also one of the factors that improves the grain growth of the KNN pellet samples which can be observed in Figure 6(c) for the samples calcined at 750 °C for 2 hours and sintered at 1100 °C.

4.0 CONCLUSION

It is observed that 750 C is the correct calcination temperature whereas 6 hours calcination time is the most appropriate as suitable calcination temperature for the solid-state synthesis of KNN. A structural analysis of the sample calcined at 750 °C for 6 hours possessed the most score of KNN compound with monoclinic crystal structure with a few secondary phases. Further sintering at 1060 °C for 2 hours shows the KNN with good stoichiometric composition of $(K_{0.507}Na_{0.537})NbO_3$ without secondary phase. The crystal structure obtained for this sample is orthorhombic. The sintering of KNN contributed to a higher density of 87.13 % densification. This is also evidenced by the SEM micrography.

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