Jurnal
Teknologi

Full Paper

INFLUENCE OF DOUBLE CALCINATION-MILLING ROUTE ON THE STRUCTURAL AND MICROSTRUCTURAL PROPERTIES OF LEAD-FREE $K_{0.5}NA_{0.5}NBO_3$ (KNN) CERAMICS

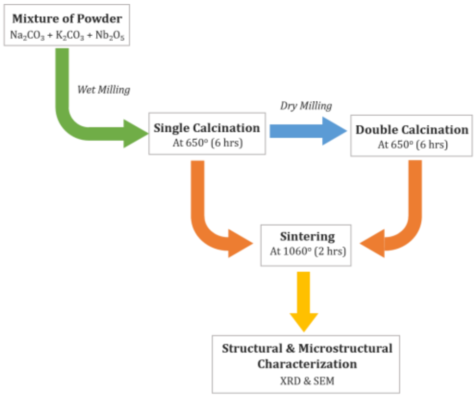
Article history
Received
14 September 2022
Received in revised form
8 February 2023
Accepted
21 February 2023
Published Online
19 April 2023

Norni Hidayawati Mat Daud[a]*, Dzetty Soraya Abdul Aziz[a], Idza Riati Ibrahim[a], Dayang Salyani Abang Mahmod[b], Amir Azam Khan[c], Nor Amalina Ahmad[a], Nurul Aisyah Farhani Mohd Fuad[b]

[a]Centre for Pre-University Study, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia
[b]Faculty of Engineering, Universiti Malaysia Sarawak, 94300 Kota Samarahan, Sarawak, Malaysia
[c]School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology (NUST), Islamabad, Pakistan

*Corresponding author
mdnorni@unimas.my

Graphical abstract



Abstract

Potassium sodium niobate (KNN) has always been one of the most potential candidates to replace lead-based piezoelectric ceramics due to its strong piezoelectric properties and environmentally friendly composition. A strong piezoelectric property is constantly influenced by the sample's densification as well as its microstructural characteristics. One of the current main issues with this KNN lead-free piezoelectric material is the difficulty in creating high-density samples by conventional preparation and sintering. Thus, KNN lead-free ceramics were synthesised using an improved solid-state method by introducing the double calcination-milling route to this process. The outcome demonstrates that, despite the presence of additional KNN secondary phases, the double calcination-milling approach contributed to the early creation of the KNN phase. When sintered pellets are subjected to a double calcination milling process, the XRD pattern revealed that the main peaks of the sample are indexed to orthorhombic $K_{0.5}Na_{0.5}NbO_3$. The double calcination KNN pellet have a relative density of 90% densification which is slightly higher than that of single calcination KNN pellet which shows 88% densification.

Keywords: Potassium Sodium Niobate, piezoelectric ceramic, double calcination, solid state method, sintering

Abstrak

Kalium Natrium Niobat (KNN) sentiasa menjadi salah satu bahan paling berpotensi untuk menggantikan seramik piezoelektrik yang berasaskan plumbum kerana sifat piezoelektriknya yang kuat dan komposisinya yang mesra alam. Sifat piezoelektrik yang kuat sentiasa dipengaruhi oleh ketumpatan sampel serta ciri mikrostrukturnya. Salah satu isu utama bahan piezoelektrik bebas plumbum KNN ini ialah kesukaran untuk menghasilkan sampel yang berketumpatan tinggi melalui kaedah dan pensinteran konvensional. Sehubungan itu, seramik tanpa plumbum KNN telah dihasilkan menggunakan kaedah keadaan pepejal yang lebih berkesan iaitu dengan

85:3 (2023) 75–81 | https://journals.utm.my/jurnalteknologi | eISSN 2180–3722 | DOI:
https://doi.org/10.11113/jurnalteknologi.v85.19202 |

memperkenalkan kalsinasi berganda kepada proses ini. Hasilnya menunjukkan bahawa, walaupun terdapat fasa sekunder KNN, pendekatan kalsinasi berganda menyumbang kepada pembentukan awal fasa KNN. Pelet yang disinter melalui proses kalsinasi berganda menunjukkan puncak utama corak XRD diindeks kepada ortorombik $K_{0.5}Na_{0.5}NbO_3$ dan pelet tersebut mempunyai ketumpatan relatif 90%, iaitu lebih tinggi daripada pelet yang disinter melalui proses kalsinasi tunggal yang mempunyai ketumpatan relatif sebanyak 88%,

Kata kunci: Kalium Natrium Niobat, seramik piezoelectric, kalsinasi berganda, kaedah keadaan pepejal, pensinteran

1.0 INTRODUCTION

Piezoelectric materials acquire the capability of producing the direct piezoelectric effect or producing the inverse piezoelectric effect. They can generate an electric potential in response to mechanical stress or generate mechanical movement when exposed to an electric field [1]. Piezoelectric materials have been used in numerous applications, especially in the disciplines of information and communications, medical diagnostics, industrial automation, etc. Sensors, transducers, ultrasonic motors, and imaging devices are examples of typical applications [2, 3].

Even though lead (Pb) is dangerous to human health and the environment, the majority of piezoelectric devices, such as transducers and actuators, employ Pb-based piezoelectric ceramics as one of its primary components [4]. The search for lead-free goods was sparked by this problem. Ceramics based on perovskite $K_{0.5}Na_{0.5}NbO_3$ (abbreviated as KNN) have been identified as one of the most promising replacement options. Due to its strong piezoelectric characteristics, the potassium sodium niobate system is of special interest.

KNN may be synthesised using several different techniques, including hydrothermal, microwave, hot press, sol-gel, and many others [5, 6, 7]. The majority of these methods have been enhanced to produce structures with exceptional piezoelectric characteristics. Typically, carbonates or oxides are used as the starting ingredients in the solid-state reaction (SSR) process to create KNN polycrystalline powders. This method's popularity is a result of how affordable it is.

Because there is a greater likelihood of the alkali elements evaporating, particularly at high temperatures, working with KNN-raw starting materials presents certain challenges, particularly with regard to maintaining the stoichiometry throughout powder production, calcination, and sintering of the pellet [8]. In this instance, a perovskite phase must develop at a minimum temperature of 850 ˚C in order for the mixture's constituent parts to have enough thermal energy to break through atomic/ionic diffusion barriers and retain the KNN stoichiometry [9].

The low-temperature calcination process is the solution to the off-stoichiometry issue for the synthesised KNN powder, as Popovic *et al*. have thermodynamically demonstrated that the temperature increase from 627 °C to 927 °C led to an increase in the vapour pressure of alkali elements over the respective niobates by 4 to 5 orders of magnitude [10]. The problem of the alkali elements evaporating at high temperatures may be solved by low temperature synthesis.

Additionally, KNN synthesised at lower calcination temperatures of 650 °C and 750 °C has an excellent stoichiometric composition, according to the findings of Ahmad *et al*. [12]. The combination does not, however, exhibit particularly strong densification. One of the current main issues with this KNN lead-free piezoelectric material is the difficulty in creating high-density samples by conventional preparation and sintering. The purpose of this study is to ascertain if the twofold calcination-milling method can further homogenise the particle size distribution of the pre-sintered powders, resulting in grains with greater homogeneity and compatibility, and so enhancing the densification of the synthesised KNN.

2.0 METHODOLOGY

$K_{0.5}$ $Na_{0.5}NbO_3$ (KNN) powders were synthesized by a conventional solid-state reaction method using sodium carbonate, Na_2CO_3, (Merck, 99 % purity), potassium carbonate, K_2CO_3 (Merck, 99 % purity) and niobium oxide, Nb_2O_5 (Sigma Aldrich, 99% purity) as the starting precursors.

These three powders were first dried separately for two hours at 200 °C in an oven before being weighed using the stoichiometric formula in equation (1).

$$K_2CO_3 + Na_2CO_3 + 2Nb_2O_5 \rightarrow 4K_{0.5}Na_{0.5}NbO_3 + 2CO_2 \quad (1)$$

The powders were then added to a tungsten carbide jars (50 ml) equipped with tungsten carbide balls and a ball-to-powder mass ratio (BPR) of 10:1 was used. The jars were then filled with 40 ml acetone to act as the dispersant. In a planetary ball mill, the powders were combined and wet ground for three hours at a speed of 300 rpm. The powders were thoroughly blended and their particle sizes were decreased using the planetary ball mill [12].

To remove the acetone solution, the wet milling slurry was sieved and dried at 120°C for 2 hours [13]. For 30 minutes at 300 rpm, the dried slurry was dry-milled once more to disintegrate the agglomerates left over from the initial milling.

The powders were dried again at 120°C for 1 hour in order to remove some moisture that was absorbed by the powders during previous milling process since the powders were able to absorb moisture easily. The powders were then calcined at a temperature of 650°C for 6 hours. The obtained powders that underwent single calcination-milling route were abbreviated as C1.

Powders were handled using the same batch size and under the same circumstances as C1 for the double calcination-milling procedure. Then, the powders were ball-milled again for 3 hours at a speed of 300 rpm, and dried at 120°C for an hour. The powders were then subjected to a second calcination at 650 °C for an additional 6 hours (the powders obtained were abbreviated as C2).

X-Ray Diffraction (XRD) analysis were conducted using an X-Ray Diffractometer (PW 3040/60 MPD X'pert High Pro PANalytical) with a measuring condition of 2θ ranging from 20° to 80°. The XRD was conducted after calcination to determine the presence of KNN phase at calcination stage. The morphology of C1 and C2 powders were further analysed using a Scanning Electron Microscope (SEM) Hitachi TM3030. The particle size was determined by the line intercept method of more than 150 particles per sample and the analysis was carried out by *Image J* software.

Later, C1 and C2 powders were cold-pressed into a 15 mm diameter pellet with a thickness of 2.5 mm using a hydraulic press machine at 25 MPa. The pelletized green bodies were sintered in ambient condition using the heating rate of 5°C/min for 2 hours at 1060°C. The sintered C1 is abbreviated as SC1 while the sintered C2 is abbreviated as SC2.

The sintered pellets' structural composition was re-determined using XRD measurements, and their microstructural characteristics were analysed using SEM analysis. A densitometer was also used to test the sintered pellets' density (Mettler Toledo TLE 204).

3.0 RESULTS AND DISCUSSION

3.1 Structural Analysis

(a) Single and Double Calcination

Figure 1 shows the XRD patterns of C1 and C2 powders after the first and second calcinations at 650°C, respectively. By using the Xpert High Score PANalytical analysis, it confirms that the KNN phase has already been formed after the first step of calcination as most of the peaks matched well with orthorhombic $K_{0.507}$ $Na_{0.537}NbO_3$ phase as shown in Figure 1 (a). However, the reaction was incomplete as one diffraction peak was matched with $NaNb_3O_8$ at 2θ: 29.38°. As the powders going through the double calcination process, other peaks with different KNN stoichiometric ratio appeared and they were indexed to $K_{0.4}$ $Na_{0.6}NbO_3$, $K_{0.65}$ $Na_{0.35}$ NbO_3 and $K_{0.02}$ $Na_{0.98}$ NbO_3 as shown in Figure 1 (b). The higher intensity of the C2 peaks as compared to C1 peaks indicated the higher crystallinity of the double-calcined powders. Based on the results, both C1 and C2 showed the presence of KNN, however, C1 showed the incomplete KNN phase formation which represented by $NaNb_3O_8$ which is in agreement with the previous reported article [11]. While when subjected to double calcination (C2 sample), the peak at the particular position has been transformed to KNN phase with a stoichiometric ratio of $K_{0.4}$ $Na_{0.6}NbO_3$. This shows that double calcination process has aided the formation of KNN despite the existence of other KNN secondary phases.

(b) Sintering

Figure 1 (c) and Figure 1 (d) show the XRD patterns of SC1 and SC2 pellets after sintering, respectively. It is obvious that the peaks sharpened after sintering which indicates a more homogeneous and crystalline structure. As the pellet was sintered to 1060°C for 2 hours, the intensity of the peaks increases which also implies the growth of crystallites. The absence of $NaNb_3O_8$ in SC1, reveals the existence of pure orthorhombic phase of KNN as shown in Figure 1 (c). As for SC2 pellet, the XRD pattern shows a polycrystalline structure with the existence of secondary KNN phases: $K_{0.4}$ $Na_{0.6}NbO_3$, $K_{0.65}$ $Na_{0.35}$ NbO_3 and $K_{0.02}$ $Na_{0.98}$ NbO_3. However, the existence peaks in SC2 are still dominated by the main $K_{0.507}$ $Na_{0.537}NbO_3$ phase. This result shows that the earlier double calcination process has affected the phase formation of sintered sample. Previously, Feizpour also reported that the sintered sample processed from double-calcined KNN powder at 625 °C consist of a non-KNN secondary phase even-though the sample was placed in a double-crucible and surrounded by KNN packing powder during the air sintering process [8]. And as for sample SC2, the KNN secondary phases have been appeared starting from the double calcination process, and the XRD peak for these phases becomes sharper and its intensity is increasing showing that the KNN secondary phases is a stable phase. The existence of the secondary phases is somewhat expected in double calcination and sintering process since the raw materials for the solid-state synthesis which are generally alkali carbonates have hygroscopic nature, thus resulting in poor purity. Therefore, when the sample was subjected to double calcination and sintering, the deviations in KNN stoichiometry might occur due to uneven volatilization of the alkali oxides (Na_2O and K_2O) takes place as a result of their relatively high volatility [6] due to twice calcination and milling. It is suggested that to achieved a pure orthorhombic phase of KNN with higher densification, the sintering atmosphere should be controlled as this sintering atmosphere could affect the existence of oxygen vacancies in KNN based ceramics [14,15].

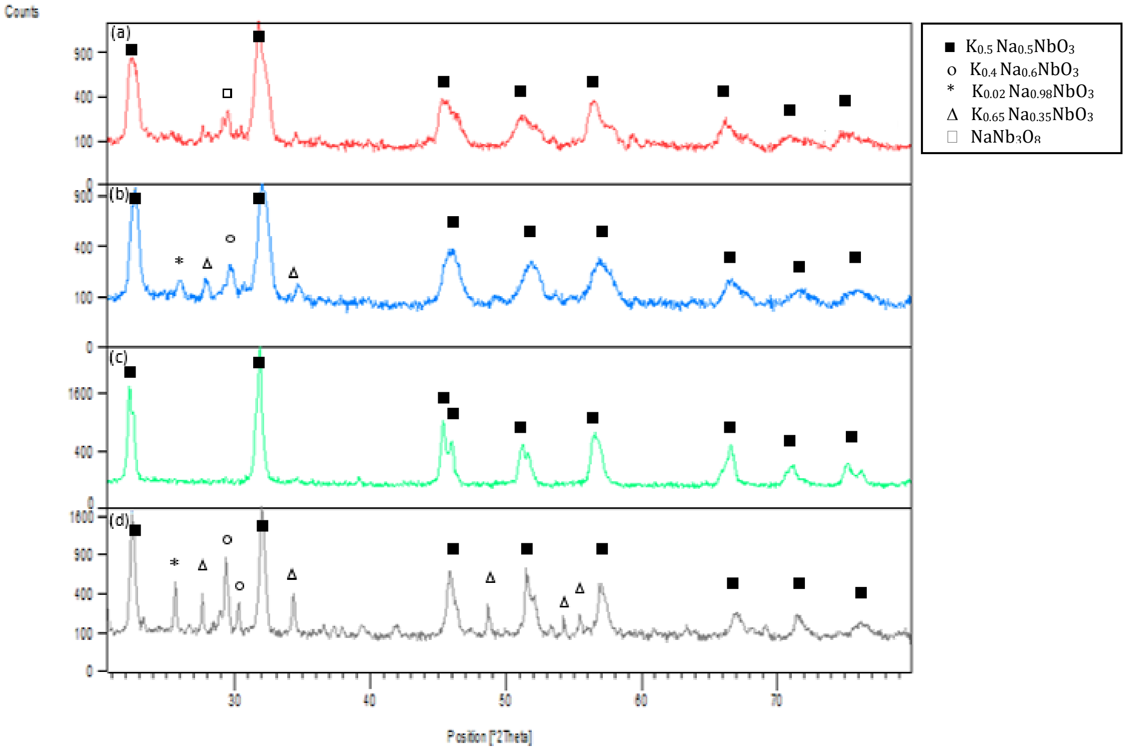


Figure 1 XRD pattern of : (a) C1, KNN single calcined powders. (b) C2, KNN double calcined powders, (c) SC1 sintered KNN pellet, (d) SC2, sintered KNN pellet

3.2 Microstructural Analysis

(a) Single and Double Calcination

The effect of single and double calcination-milling route on the surface morphology of KNN were analysed using SEM. The SEM micrographs of the mixture precursors prepared before and after calcination process are depicted in Figure 2 (a-c). The mixture of raw powders before calcination process shows inhomogeneous morphology with agglomerated particles. As going through single calcination-milling route, the powders remain clumping together but the grains appear to be more homogeneous. A better morphological structure was displayed for powders undergoes double calcination-milling route. The microstructure shows a polyhedral morphology with a lot of ultrafine particles which can be observed in Figure 2c

The particles were not densely packed, and the existence of voids between them showed that the solid-state reaction of calcined powder was still taking place [16]. The particle size distributions in Figure 2d shows a more uniform particle size distribution in double calcined sample where unimodal particle size distribution was observed unlike the single calcined sample. Particle size distributions have an important role in packing density which affects sintering [17]. Average particle sizes of single calcined and double calcined shows slightly different values which are 0.37 and 0.42 µm respectively. However, based on the particle size distribution, the particle size of double calcined shifted to larger particles where the amount of larger submicrometer particle powders increased. It is expected for the particle size in double calcined sample to exhibit larger particles as the powder was subjected to double milling and double calcination.

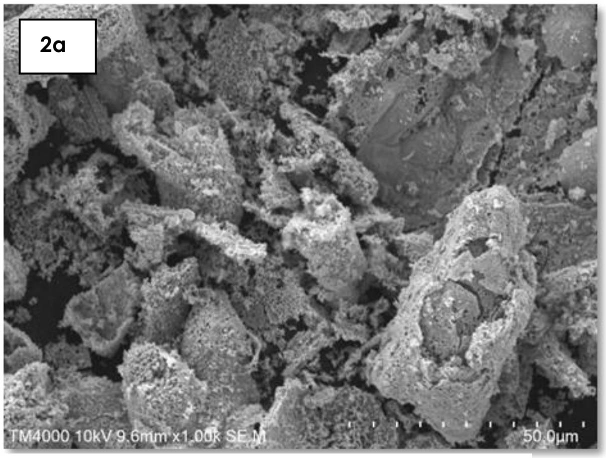


Figure 2 (a) Mixture powders before calcined

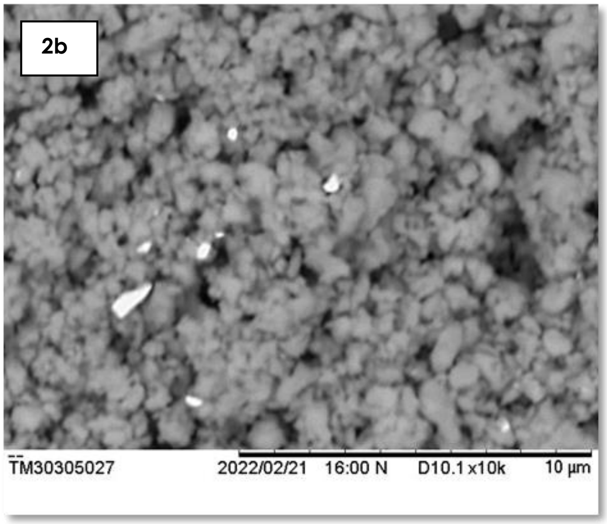


Figure 2 (b) Mixture powders after single calcined, C1

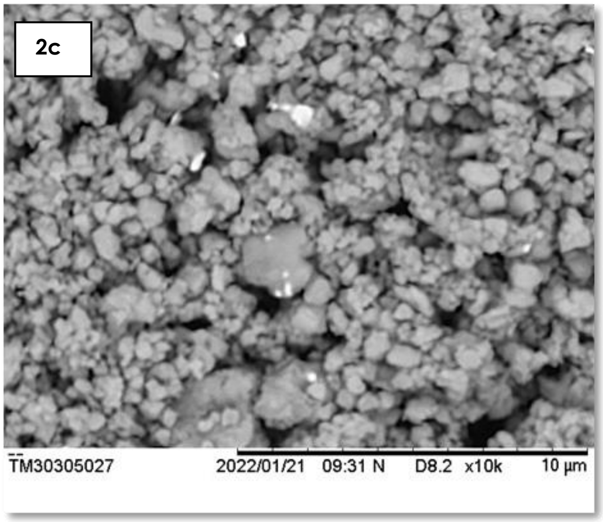


Figure 2 (c) Mixture powders after double calcined, C2

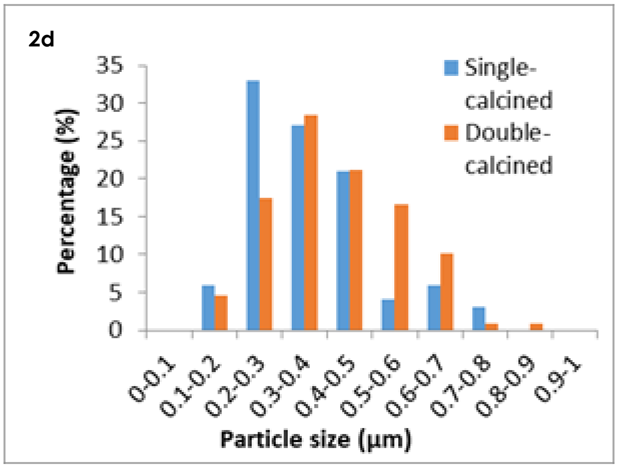


Figure 2 (d) Particle size distribution of single and double calcined

(b) Sintering

SEM results shows fairly dense microstructure and clear grain boundaries for both KNN pellet (single and double calcination-milling route) after sintering process as shown in Figure 3. The morphological structure of single calcination KNN pellet after sintering process shows the grains with hexagonal shape grows at non uniform distribution of grain sizes as shown in Figure 3 (a). These grains ranging from 0.48 to 3.08 µm with an average grains size of 1.3 µm appears more visible in the high magnification images as shown in Figure 3 (a). The small grains seem to fill in the gap between the larger grains causes less porosity detected in the microstructure. Meanwhile, KNN undergoes double calcination process shows a more uniform grains with larger grain size ranging from 0.98-4.10 with an average of 2.32 µm. It shows that the ultrafine particles form during the double calcination process have completely react with each other in the sintering process. The grains form a cuboidal shape and the grain size is larger compared to the KNN pellet undergoes single calcination process, with a slight porosity which is shown by the small black area between the grains in Figure 3 (b) [18,19].

The grain size distribution for SC1 and SC2 can also be observed in Figure 3 (c). Figure 3 (c) shows the grain size distribution of KNN pellet undergoes double calcined process tends to shift to larger grains where the amount of larger submicrometer grains increased. Meanwhile grain size distribution of KNN pellet undergoes single calcination process shifted to smaller grain size region, showing that SC1 pellet possessed larger number of smaller grains as compared to SC2. As the SC2 sample is initially subjected to double milling, the diffusion area and free surfaces would be enlarged, resulting in enhancement of the diffusion kinetics when subjected to sintering. As the diffusion kinetics is higher in double calcination sample, it is observed that the presence of the pores is lesser in volume but larger in size compared to the single calcined KNN pellet. This is because, the intergranular pores would be combined through grain boundary diffusion in which the particles moved closer to form grains. Then, the pores close to and on grain boundaries were slowly eliminated generally by diffusion of vacancies from the pores along grain boundaries with densification of the sample [19,20], resulting in the reduced number of pores in double calcination sample. In this case, the density of SC2 can be denser compared to SC1 since the volume of pores is less or insignificant.

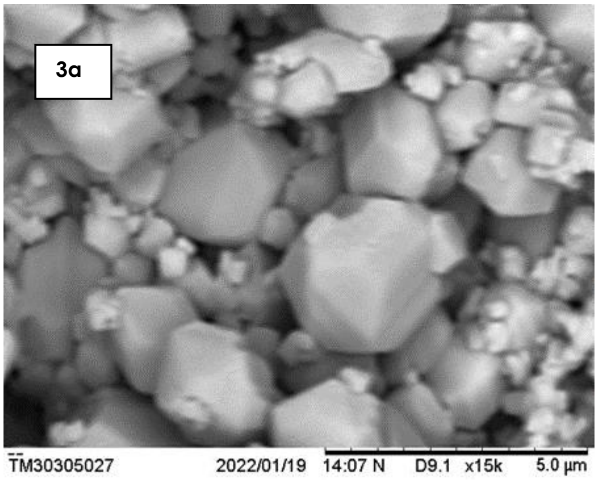


Figure 3 (a) Single calcination KNN pellet after sintering, SC1

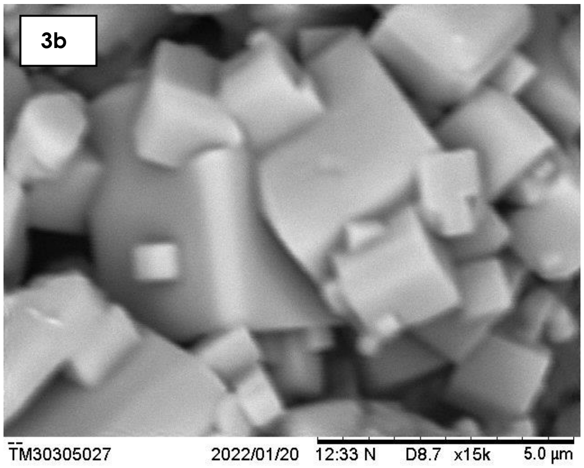


Figure 3 (b) Double calcination KNN pellet after sintering, SC2

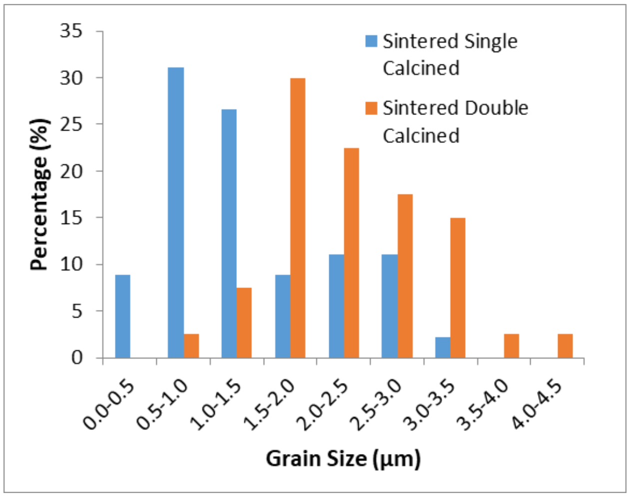


Figure 3 (c) Grain size distribution of sintered single calcination pellet, SC1 and sintered double calcination pellet, SC2.

3.3 Relative Density Analysis

The density of the KNN pellets after sintering, SC1 and SC2, respectively was measured using a densitometer. It shows that the relative density of sintered KNN pellet undergoes single calcination process, SC1 reached 88% of theoretical density while for sintered KNN pellet undergoes double calcination process, SC2, the relative density is higher which achieved 90%. The results are consistent with the SEM micrograph which shows that the larger grain size with only slight pores in the SC2 contribute to a denser compound.

The single calcination does not contribute enough to reduce the number of pores which leads to the lower density of the material. Therefore, double calcination was introduced to overcome the lower density of the material. It is important to achieve higher density since the lower density material through single calcination would possess higher pores that decreases the chemical stability and mechanical strength of the material. The dielectric breakdown would also occur during polarization causes by the concentrated electric field at the excessive pores [21]. By using the double calcination route method, improved piezoelectric properties can be obtained due to the improvement of densification through the elimination of the porosity in the samples [22].

4.0 CONCLUSION

$K_{0.5}Na_{0.5}NbO_3$ was effectively synthesised by enhancing the solid-state reaction technique utilising the double calcination-milling process. It demonstrates that KNN goes through a second calcination milling method, which results in improved shape and increased density, both of which potentially help to increase piezoelectric property. This double calcination milling route also has aided to the formation of orthorhombic KNN phase despite the existence of other KNN secondary phase. Controlling the sintering environment during the sintering process is recommended as a way to enhance the twofold calcination-milling route approach and produce a single phase KNN with a greater densification.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

Acknowledgement

This research is fully supported by SGS grant, (C09/SGS/1944/2020). Support from the Centre of Pre-University and Faculty of Engineering, Universiti Malaysia Sarawak and Faculty of Science and Technology, Universiti Kebangsaan Malaysia are also acknowledged.

References

[1] Hao, J., Li, W., Zhai, J., and Chen, H. 2019. Progress in High-strain Perovskite Piezoelectric Ceramics. *Materials Science and Engineering R: Reports*. 135: 1-57. Doi:10.1016/j.mser.2018.08.001.

[2] Kumar, A., Sharma, A., Kumar, R., Vaish, R., Chauhan, V. S., and Bowen, C. R. 2015. Piezoelectric Materials Selection for Sensor Applications using Finite Element and Multiple Attribute Decision-making Approaches. *Journal of Advanced Dielectrics*. 5(1). Doi:10.1142/S2010135X15500034.

[3] Moriana, A. D., and Zhang, S. 2018. Lead-free Textured Piezoceramics using Tape Casting: A Review. *Journal of Materiomics*. 4(4): 277-303. Doi:10.1016/j.jmat.2018.09.006.

[4] Izzuddin, I., Mohammad, M. H., Zainuddin, Z., and Janil, N. H. 2019. Piezoelectric Enhancements in $K_{0.5}Na_{0.5}NbO_3$-based Ceramics via Structural Evolutions. *Ceramics International*. 45(14): 17204-17209. Doi:10.1016/j.ceramint.2019.05.275.

[5] Khorrami, G. H., Kompany, A., and Khorsand Zak, A. 2013. A Facile Sol-gel Approach to Synthesize KNN Nanoparticles at Low Temperature. *Materials Letters*. 110: 172-175. Doi:10.1016/j.matlet.2013.07.115.

[6] Piskin, C., Karacasulu, L., Bortolotti, M., and Vakifahmetoglu, C. 2021. Synthesis of Potassium–sodium Niobate (KNN) from NbO_2. *Open Ceramics*. 7. Doi:10.1016/j.oceram.2021.100159.

[7] Li, H., Hao, Y., Lin, Z., *et al*. 2022. (K,Na)NbO_3 Lead-free Piezoceramics Prepared by Microwave Sintering and Solvothermal Powder Synthesis. *Solid State Communications*. 353: 114871. Doi:10.1016/J.SSC.2022.114871.

[8] Feizpour, M., Ebadzadeht, T., and Jenko, D. 2015. Solid-state Sintering of (K0.5Na0.5)NbO3 Synthesized from an Alkali-carbonate-based Low-temperature Calcined Powder. *Materiali in Tehnologije*. 49(6): 975-982. Doi:10.17222/mit.2015.315

[9] Rani, R., Sharma, S., Quaglio, M., *et al*. 2017. A Novel Low Temperature Synthesis of KNN Nanoparticles by Facile Wet Chemical Method. *Materials Sciences and Applications*. 08(03): 247-257. Doi:10.4236/msa.2017.83017.

[10] Popovič, A., Bencze, L., Koruza, J., and Malič, B. 2015. Vapour Pressure and Mixing Thermodynamic Properties of the $KNbO_3$-$NaNbO_3$ System. *RSC Advances*. 5(93): 76249-76256. Doi:10.1039/c5ra11874c.

[11]. Quintero, M. C., Rincón, M., Osorio-Guillén, J. M., López, D., and Londoño-Badillo, F. A. 2019. Grinding Methods Effects on the Synthesis of Potassium-Sodium Niobate Powders by Oxide Mixing. *TecnoLógicas*. 22(46): 15-23. Doi:10.22430/22565337.1269.

[12] Ahmad, N. A., Aziz, D. S. A., Daud, N. H. M., Noor, R., and Khan, A. A. 2020. Synthesis and Characterization of Lead-free Piezoelectric $(K_{0.5}Na_{0.5})NbO_3$ Produced with Improved Calcination Temperature. *Jurnal Teknologi*. 82(2): 139-147. Doi:10.11113/jt.v82.13992.

[13] Wei, N., Wang, J., Li, B., Huan, Y., and Li, L. 2015. Improvement of the Piezoelectric and ferroelectric Properties of $(K, Na)_{0.5}NbO_3$ Ceramics via Two-step Calcination-milling Route. *Ceramics International*. 41(8): 9555-9559. Doi:10.1016/j.ceramint.2015.04.015.

[14] Zhang, N., Zheng, T., and Wu, J. 2020. Lead-Free (K,Na)NbO_3-based Materials: Preparation Techniques and Piezoelectricity. *ACS Omega*. 5(7): 3099-3107. Doi:10.1021/acsomega.9b03658.

[15] Li, B. Y., Chen, X. M., Liu, M. D., Yu Z. De., Lian, H. L., and Zhou, J. P. 2021. Improved Ferroelectric and Piezoelectric Properties of $(Na_{0.5}K_{0.5})NbO_3$ Ceramics via Sintering in Low Oxygen Partial Pressure Atmosphere and Adding LiF. *Journal of Advanced Dielectrics*. 11(2). Doi:10.1142/S2010135X21500120.

[16] Nandini, R. N., Krishna, M., Suresh, A. V., and Narasimha Rao, K. 2018. Effect of Calcination Kinetics and Microwave Sintering Parameters on Dielectric and Peizo-electric Properties of (K0.5Na0.5) NBO3 Ceramics. *Iranian Journal of Materials Science and Engineering*. 15(2): 14-31. Doi:10.22068/ijmse.15.2.14.

[17] Gul, M., Gurbuz, M., Gokceyrek, A. B., Toktas, A., Kavas, T., and Dogan, A. 2020. Influence of Particle Size and Sintering Temperatures on Electrical Properties of $0.94Na_{0.5}Bi_{0.5}TiO_3$-$0.06BaTiO_3$ Lead Free Ceramics. *Archives of Metallurgy and Materials*. 65: 609-614. Doi:10.24425/amm.2020.132799.

[18] Dávila, L. F., Quintero, M. C., and Londoño, F. A. 2021. Influence of Synthesis Process on the Structural and Microstructural Behavior of Neodymium Doped Sodium and Potassium Niobate Powders. *Journal of Physics: Conference Series*. 2046(1). Doi:10.1088/1742-6596/2046/1/012054.

[19] Malič, B., Koruza, J., Hreščak, J., *et al*. 2015. Sintering of Lead-free Piezoelectric Sodium Potassium Niobate Ceramics. *Materials*. 8(12): 8117-8146. Doi:10.3390/ma8125449.

[20] Ye, G., Wade-Zhu, J., Zou, J., Zhang, T., Button, T. W., and Binner, J. 2020. Microstructures, Piezoelectric Properties and Energy Harvesting Performance of Undoped $(K_{0.5}Na_{0.5})NbO_3$ Lead-free Ceramics Fabricated via Two-step Sintering. *Journal of the European Ceramic Society*. 40(8): 2977-2988. Doi:10.1016/j.jeurceramsoc.2020.02.035.

[21] Ohbayashi, K. 2016. Piezoelectric Properties and Microstructure of (K,Na)NbO_3–$KTiNbO_5$ Composite Lead-Free Piezoelectric Ceramic. Piezoelectric Materials http://dx.doi.org/10.5772/62869.

[22] Ji, Jae-Hoon, Moon, Un-Chul, Kwon, Hyuck-In, Koh, Jung-Hyuk. 2017. The Two-step Sintering Effect on the Dielectric and Piezoelectric Properties of (Na,K)NbO_3-$BiScO_3$ Lead-free Ceramics. *Ceramics International.* 43. Doi:10.1016/j.ceramint.2017.05.237.