EFFECT OF DIFFERENT COMPACTION PRESSURE AND DIFFERENT SINTERING ROUTE ON $K_{0.5}Na_{0.5}NbO_3$ PHYSICAL AND DIELECTRIC PROPERTIES

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Alkaline niobate known as $K_{0.5}Na_{0.5}NbO_3$ (KNN), a lead-free piezoelectric ceramic was synthesized via a solid state reaction method. The samples were compacted at different pressures (100, 200, 300 and 400 MPa) and sintered using two different techniques (conventional furnace and hot isostatic pressing (HIP)). The effect of compaction pressure and sintering technique on physical and dielectric properties was studied. The optimum compaction pressure (300 MPa) and sintering via HIP (at 1080°C for 30 min) increased the density and grain size (range 30 - 300 nm) and improved its dielectric properties. Therefore, the combination of suitable compaction pressure and sintering technique has produced larger grain size and higher density of KNN which resulted in outstanding dielectric properties. At room temperature, excellent values of ε_r (5517.35) and tan δ (0.954), recorded at 1 MHz were measured for the KNN300HIP sample with highest density (4.4885 g·cm^{-3}).

INTRODUCTION

Piezoelectric materials are widely used for many applications, especially in the fabrication of actuators, sensors and transducers. Most of these piezoelectric devices using lead-based perovskite-type single crystals or piezoelectric ceramics such as $Pb(ZrTi)O_3$ [1-9]. Lead Zirconate Titanate (PZT) which consists of more than 60 wt. % of Pb, has been widely used in electronic devices because of its excellent piezoelectric properties. However, due to their high toxicity effects, there are many restrictions on using certain lead-containing materials in order to protect environment and human health [3, 10-11]. However, lead-free alternatives to PZT have been developed, which currently dominated the market of piezoelectric materials. Among them alkaline niobates $(K_xNa_{1-x})NbO_3$, known as KNN ceramics, are the most investigated.

The most widely used compound of KNN which derived from solid solution between $KNbO_3$ (KN) and $NaNbO_3$ (NN) is $K_{0.5}Nb_{0.5}NbO_3$ ($x = 0.5$). This is due to its near morphotropic phase boundary between two orthorhombic structures. KNN is a good candidate compare to other lead free piezoelectric materials such as barium titanate ($BaTiO_3$) because of its high Curie

temperature and good piezoelectric properties. The addition of KN to NN results in a ferroelectric phase with a high T_c (exceeding 400°C) and is accompanied by a decrease in critical electric field needed to induce a ferroelectric phase transition [12]. High T_c is required for high-temperature applications since the dielectric and piezoelectric properties are highly dependent on their T_c value [13]. However, the main problem faced by KNN is the difficulty to obtain a high-density body, especially when fabricated via conventional ceramic processing routes due to the higher volatility of potassium (K) and sodium (Na) at high temperature, causing deviations from its stoichiometry [14-15]. Apart from that, the hygroscopic carbonate precursors (K_2CO_3 and Na_2CO_3), will cause the sample to absorb water from the surroundings interfering with the sample weighing process. Many studies have been carried out in order to improve the piezoelectric properties of KNN-based ceramics. These include chemical modification to prepare compositions close to an MPB or the shift of the orthorhombic to tetragonal phase transition (T_{O-T}) to near or below room temperature, such as KNN–(Li, K, Ag) [16], KNN–Ag(Nb, Sb, Ta)O_3 [17], KNN–($Bi_{0.5}Na_{0.5}$) TiO_3 [18] and also adding sintering aids like MnO_2 and WO_3 [19] to achieve higher density of the final product.

Unfortunately, the improvement of their piezoelectric properties is usually accompanied by the reduction of T_c and also reduces the operational temperature of electrical properties which limits their practical application at high-temperatures [13]. An example for high-temperature applications is in ultrasonic techniques for nondestructive testing (NDT) or non-destructive evaluation (NDE), where the pulse transit time method is used to monitor the material properties and integrity of critical structures in the temperature range 250 - 300°C [20]. Therefore, in order to achieve very high density KNN, it is important to investigate other fabrication approaches such as hot isostatic press (HIP).

The HIP technique has the ability to produce almost zero porosity bodies. Therefore, this approach can enhance the densification of KNN in order to improve their final electrical properties which without shifting of tetragonal to orthorhombic phase-transition (T_{O-T}) and the Curie temperature (T_c) took place [14]. Previous work done by Egerton and Bieling [21] using the HIP technique to sinter KNN was focused only on the preparation of transducers and no further work was done about the structural effects on their electromechanical properties [15]. For that reasons, in this research, the influence on the electromechanical properties of two different sintering methods (conventional furnace and HIP technique) to synthesize KNN ($K_{0.5}Na_{0.5}NbO_3$) was compared.

EXPERIMENTAL

$K_{0.5}Na_{0.5}NbO_3$ was synthesized using the solid state reaction method. A mixture of K_2CO_3 (System-ChemAR, 99.5 %), Na_2CO_3 (Bendosen, 99.8 %), and Nb_2O_5 (Merck, 99 %) were used in this research as starting raw materials. The raw materials were dried at 200°C for 1 hour in an oven in order to eliminate hygroscopic nature which bound with water. The raw materials were then weighed and mixed in a ball mill using ZrO_2 balls in ethanol medium for 24 hours, then dried and calcined at 800°C for 4 hours with a heating rate of 3°C·min^{-1}. The calcined powder was ground and mixed with 6 wt.% of polyvinyl alcohol (PVA) binder solution before uniaxially pressed at four different compaction pressures (100, 200, 300 and 400 MPa, respectively) into disks with 13 mm diameter and 2.5 mm thickness. The pellets were finally sintered by using 2 different techniques: conventional furnace sintering (Carbolite RHF 1400) at 1080°C for 2 hours and hot isostatic pressing (American Isostatic Presses, INC HP630) at similar temperature but only for 30 minutes with heating and cooling rate of 3°C·min^{-1}. The KNN samples sintered using conventional furnace have been labeled as KNN100CV, KNN200CV, KNN300CV and KNN400CV, respectively. The KNN samples sintered using hot isostatic pressing have been labeled as KNN100HIP, KNN200HIP, KNN

300HIP and KNN400HIP, respectively. The densities of the sintered pellets were measured using gas pycnometer (MicromeriticsAccupyc II 1340). X-ray diffraction (XRD) (XRD Bruker AXS D8 Advance) analysis was carried out to check the phase composition and structure. The microstructure of samples was observed by using Field Emission Scanning Electron Microscope (FESEM) (Zeiss SUPRA 35VP). The samples were coated by using silver paste electrode on both sides, and then heat treated at 143°C for 30 minutes for the dielectric measurement. The relative permittivity (ε_r) and tangent loss (tan δ) have been measured using impedance analyzer (RF Impedance/Material Analyzer 4291B Hewlett Packard) from 1 MHz to 1 GHz.

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern of KNN samples pressed at 4 different compaction pressures and sintered by two different techniques (conventional furnace and hot isostatic pressing (HIP)). All samples showed an identical peak position and peak shape. Furthermore, all samples show the formation of KNN perovskite structure and a typical orthorhombic symmetry without secondary phase, which is similar to results obtained by Wang et al. [16].
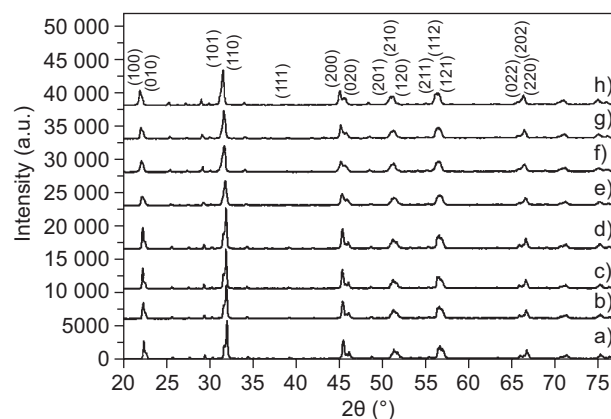

Figure 1. The XRD pattern of the $K_{0.5}Na_{0.5}NbO_3$ samples after prepared under different compaction pressures (100, 200, 300 and 400 MPa) and different sintering methods (conventional and hot isostatic pressing).

Figure 2 shows FESEM micrographs of KNN pellets sintered at 1080°C using conventional furnace (2 hours) and HIP technique (30 minutes), respectively. The trend is that as the compaction pressure increase, the grain sizes are getting larger. Besides that, by using HIP, the grain growth also occurs possibly due to the very high pressure applied from the environment which induced better contact among the particles. Plastic deformation may also contribute to better particle-particle contacts which may facilitate material transport (diffusion) and
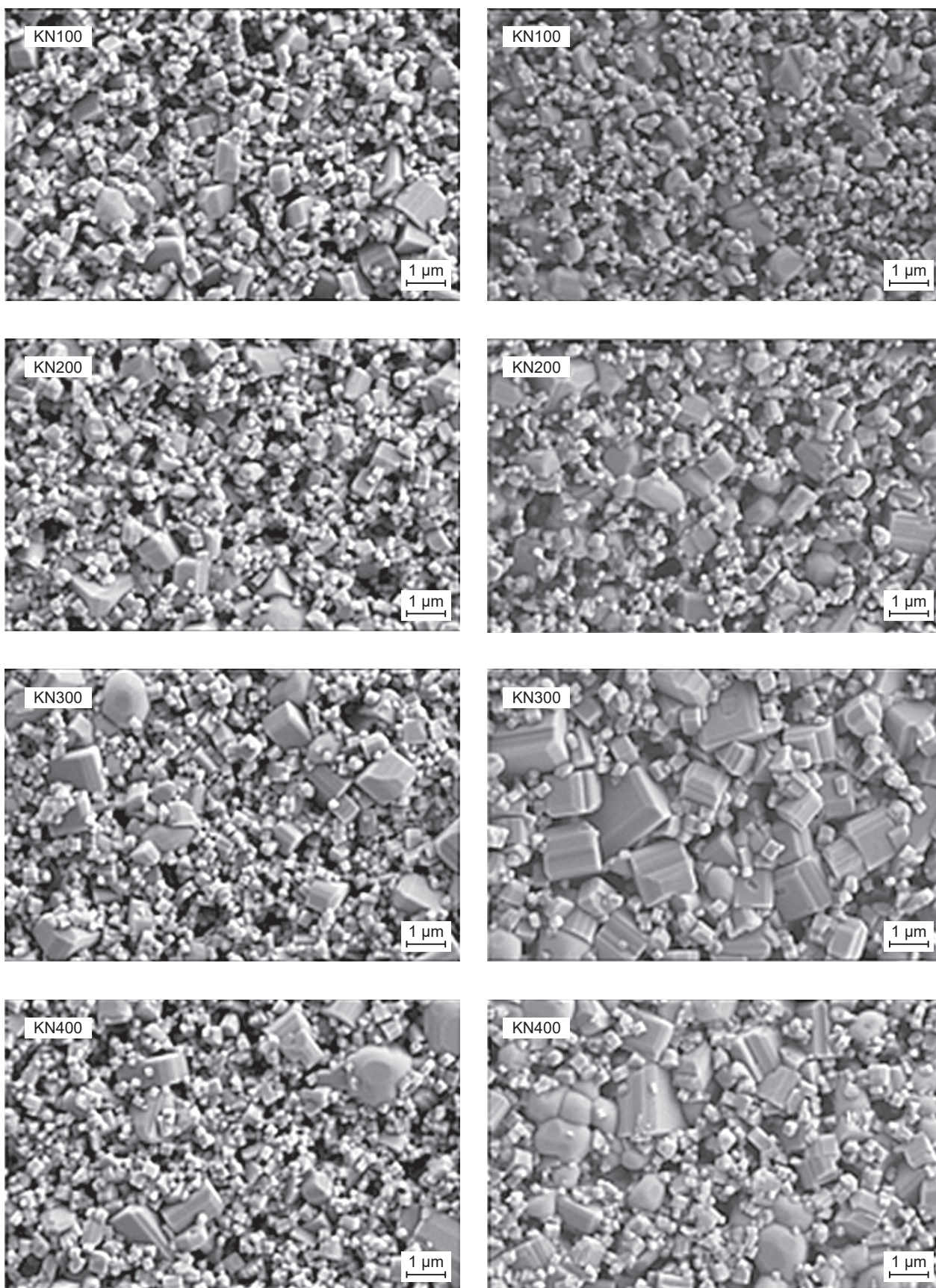
a) KNN100-400CV – 1080°C, 2 hour, 3°C·min^{-1}.

b) KNN100-400HIP – 1080°C, 30 minutes, 3°C·min^{-1}.

Figure 2. FESEM images of KNN ceramics: a) KNN100-400CV and b) KNN100-400HIP.

reactions to occur [22]. As shown in Figure 2b, the HIP technique produced a larger grain size with wider grain size distribution when compacted at 300 MPa. The grain size is far larger (30 - 300 nm) then that corresponding to the same pressure in conventional sintering furnace (10 - 150 nm). From Figure 2, even the grain size distribution observed appears quite different, but EDX analysis indicated that small and large grains had same composition (KNN). FESEM micrographs obtained are also quite similar to other researcher's results [23]. However, as the compaction pressure applied exceeded a limit (400 MPa), the average grain size started to reduce back due to the effect of very high compression, which induced cracks to the sample surface. The cracks occur due to compact's failure to fit back into die cavity after ejection and fragmentation of the sample. Because of that, the grain growth during sintering was not completely happened due to loss of energy through the present of fragmentation on the sample surface [26].

Figure 3 shows the density increasing for all samples compacted up to 300 MPa before it drops at 400 MPa. This is due to the excess pressure (400 MPa) applied during powder compaction which causes fracture on the sample surface that was connected to mould inner wall [24]. The bulk density reaches its maximum for the sample sintered using HIP technique at 1080°C for 30 minutes (4.485 g·cm⁻³) and it is 99.4 % of the theoretical density of KNN ceramics (TD = 4.51 g·cm⁻³). This trend is exactly following the morphology trends of the samples as shown in Figure 2. According to another researcher [22], by using HIP, the density of niobates ceramics has increased up to 98.9 % of theoretical density.
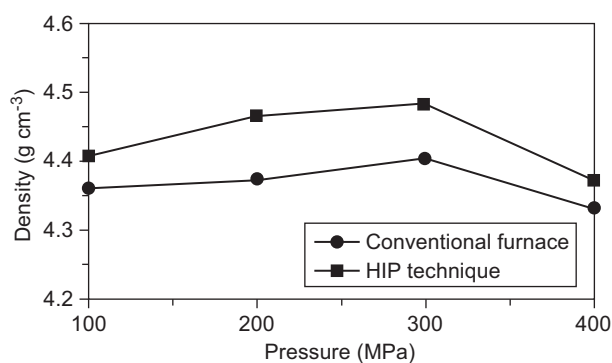

Figure 3. Density variations with four different pressures applied during powder compaction by using two different sintering technique.

Figure 4 shows the relative permittivity (ε_r) and tangent loss (tan δ) as a function of frequency for samples prepared with different sintering techniques. The results show that by using HIP, the ε_r values are higher compared to conventional sintering. The ε_r started to decrease when the compaction pressure was 400 MPa. This is due to the cracks that are present on the surface which is in contact with the mold and caused the

density decrease also current leakage can easily occur. For the same reason, the tan δ value recorded for the KNN400CV sample was the highest.

From Figure 4b, it can be observed that at low frequency the ε_r value was higher for the sample prepared by HIP. At 1 MHz, the KNN300HIP sample gave the highest value of ε_r (5517.35) and lower tan δ (0.954). However, at higher frequencies, the ε_r value tends to decrease due to a space charge relaxation process characteristic of polycrystalline materials [25, 27]. The ε_r value of samples sintered using HIP technique was higher due to a better densification of ceramics (Figure 3) compared to samples sintered using the conventional furnace. Other researchers [28] reported that the ε_r of the sample was highly dependent on the average grain size and density of the sample. The reason for the latter is that higher density of sample will provide more space for holding larger quantity of charge for a longer period of time. Since, the samples pressed at 300 MPa exhibited the highest density (Figure 3) and largest grain size (Figure 2), these samples attained excellent dielectric properties. In this study, the ε_r values observed in the KNN sample prepared using HIP are higher compared to what has
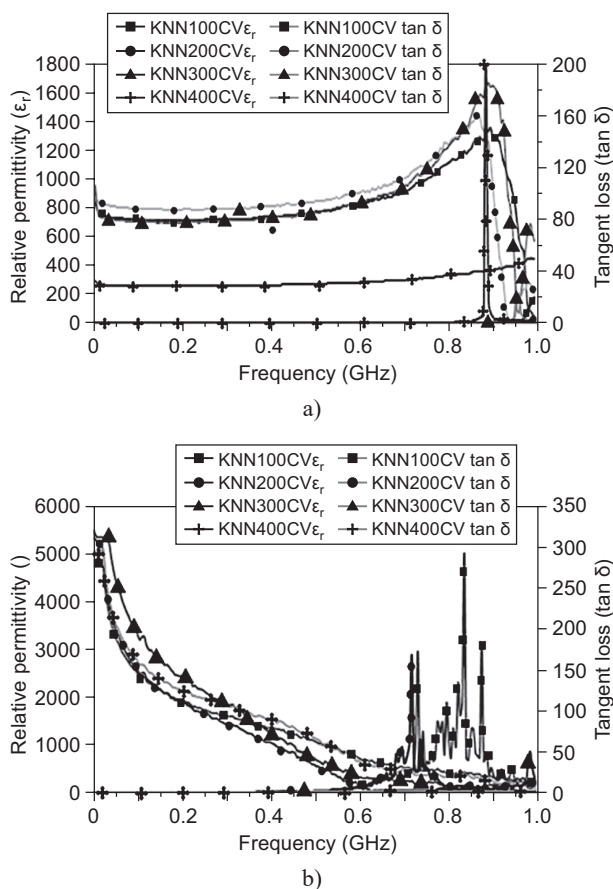

a)

b)

Figure 4. The frequency dependence of the ε_r and tan δ value for the samples that being sintered using: a) conventional furnace, and b) hot isostatic pressing (HIP) techniques.

been reported by other researchers [29-30]. The ability of the HIP technique to produce higher density and larger average grain size is the reason for better dielectric properties compared to conventional sintering.

Figure 5 shows the compaction pressure dependence of the ε_r and tan δ values for samples that sintered using (a) conventional furnace and (b) (HIP) at 1 MHz. The ε_r value obtained for KNN100-400HIP at room temperature is higher compared to the sample KNN100-400CV. The tan δ recorded at 1MHz for the sample sintered using HIP also high compared to conventional furnace sintering. The reason is that the high density and also decreasing number of grain interfaces in KNN100-400HIP compares the KNN100-400CV samples. Higher density of KNN samples provide more space for holding larger quantity of charge longer periods of time [22]. The decreasing numbers of grain interfaces resulting from the increase of grain size will encourage the domain wall motion and subsequently improve the polarization activities which affect the final dielectric properties [30].
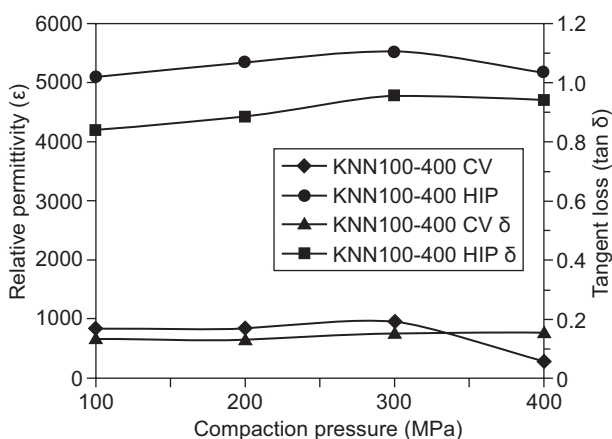

Figure 5. The variation of ε_r and tan δ value for the samples that being sintered using: a) conventional furnace and b) hot isostatic pressing (HIP).

CONCLUSION

The effect of compaction pressure and sintering technique on the phase composition, microstructure, density and dielectric properties during fabrication of $K_{0.5}Na_{0.5}NbO_3$ ceramics sample via the solid state synthesis technique was investigated. The optimum compaction pressure (300 MPa) and using hot isostatic pressing (HIP) (at 1080°C for 30 minutes) has successfully raises the density, increase grain size (30 - 300 nm), broader grain size distribution and improves the dielectric properties of $K_{0.5}Na_{0.5}NbO_3$ ceramics. The larger grain size and higher density of ceramic bodies will produce outstanding dielectric properties. At room temperature, the excellent relative permittivity and tangent loss recorded at 1 MHz (ε_r = 5517.35 and tan δ =

= 0.954), respectively for the KNN300HIP sample. The KNN300HIP sample also exhibits highest relative density (4.485 g·cm^{-3}). Therefore, hot isostatic pressing (HIP) technique is considered as a potential method to produce better KNN ceramics with excellent properties that can be used for advanced electroceramics applications.

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