

Influence of Crystal Structural Orientation on Impedance and Piezoelectric Properties of KNN Ceramic Prepared using Sol-Gel Method

(Pengaruh Orientasi Struktur Hablur ke atas Sifat Impedans dan Piezoelektrik Seramik KNN yang Disediakan menggunakan Kaedah Sol-Gel)

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ABSTRACT

The aim of this study was to investigate the effect of structural orientation on the impedance and piezoelectric properties of $Ka_{0.5}Na_{0.5}NbO_3$ (KNN) ceramic synthesized using modified sol-gel method. Dried xerogel was heated at 800°C for 90 min and the aggregates were grinded to powder form. SEM micrographs confirmed that the powder consist of bimodal particles in nm and μm size regimes. The powder was compacted into 13 mm diameter pellet and sintered at 1000°C for 6 h. Then the pellets were poled at 4.0kV/mm at 100°C for 30 min. The as-sintered pellets displayed different sizes of cuboidal granules forming a relatively dense sample. The XRD and Raman spectroscopy results confirmed the formation of perovskite KNN with monoclinic crystal structure. The compositional analysis using Vegard's law showed that the K:Na ratio was 0.5:0.5. Dramatic intensity enhancement in (110) reflection and subsequent reduction in (100) reflection as observed in X-ray diffractograms for the poled pellet suggest permanent shift in crystal orientation. Consequently, the Nyquist impedance plot of a Debye type semicircular arc was altered to a combination of a depressed semicircular arc. Unlike the initial plot, the real impedance, Z' exhibited frequency dependence at low frequency regime. In addition, the relaxation time, τ of KNN sample shifted to lower frequency after the structural re-orientation while piezoelectric constant, d_{33} along (110) direction significantly improved from 5 to 35 pC/N.

Keywords: Domain; d_{33} constant; nanosize; poling; Vegards law

ABSTRAK

Tujuan penyelidikan ini ialah untuk mengkaji kesan orientasi struktur hablur ke atas sifat elektrik impedan dan piezoelektrik bagi seramik $Ka_{0.5}Na_{0.5}NbO_3$ (KNN) yang disintesis melalui kaedah sol gel yang diubah suai. Xerogel KNN yang telah kering dipanaskan pada suhu 800°C selama 90 min dan agregat yang terhasil dikisar untuk menghasilkan serbuk KNN. Mikrograf SEM mengesahkan saiz partikel KNN yang disintesis terdiri daripada partikel bimod iaitu dalam rejim bersaiz nm dan μm . Seterusnya KNN dipadatkan ke bentuk pelet berdiameter 13 mm dan disinter pada suhu 1000°C selama 6 jam diikuti dengan pengutuban pada 4kV/mm pada suhu 100°C selama 30 min. Sampel KNN yang disinter menunjukkan pembentukan butiran kuboid pelbagai saiz yang secara relatifnya membentuk sampel yang tumpat. Hasil pencirian XRD dan Raman mengesahkan pembentukan perovskit KNN dengan struktur hablur monoklinik. Analisis komposisi menggunakan hukum Vegard menunjukkan nisbah bagi K:Na adalah 0.5:0.5. Peningkatan keamatan yang mendadak pada satah (110) dan penurunan ketara keamatan pada satah (100) seperti yang diperhatikan pada difraktogram sinar-X bagi pelet yang dikutubkan menandakan peralihan kekal terhadap orientasi hablur. Akibatnya, graf impedans Nyquist lengkungan semibulatan Debye berubah kepada gabungan lengkungan semibulatan terhimpit dan permulaan bagi lengkungan lain pada frekuensi rendah. Tidak seperti plot yang asal, graf impedan nyata, Z' adalah bebas frekuensi pada rejim frekuensi rendah. Selain itu, masa santaian, τ bagi sampel KNN berganjak kepada frekuensi yang lebih rendah selepas pengorientasi semula manakala pemalar piezoelektrik, d_{33} pada arah (110) menokok secara signifikan daripada 5 kepada 35 pC/N.

Kata kunci: Domain; hukum Vegards; pemalar d_{33} ; pengutuban; saiz nano

INTRODUCTION

Awareness on the environmental and human health has led to the evolution of new piezoelectric ceramics with main focus on synthesizing environmental friendly materials to replace the existing lead-based piezoelectric ceramics. Potassium sodium niobate ($(K_{0.5}Na_{0.5}NbO_3)$ abbreviated as KNN) based system have been considered as one of the most potential candidates as non lead-based ceramics

ever since Saito et al. (2004) claimed that composition and structure-modified KNN-based ceramics have comparable piezoelectric properties to those of PZT.

In any materials engineering, selection of preparation technique is critical. Most researchers focus their effort on solid state reaction (SSR) method to synthesize KNN-based ceramics (Hollenstein et al. 2007; Rubio-Marcos et al. 2010a; Saeri et al. 2011; Tan et al. 2012; Wongsanmai et

al. 2012, Zhengfa et al. 2011). This conventional method typically start with mixing the raw materials, followed by calcination process, then continued with pressing the powder into pellet form and finally the sintering process. Since the particle size of the raw materials SSR method are usually in μm regime, the calcined products are commonly in large grains with fairly uniform particle size distribution.

Unfortunately, large grains posed greater challenge to produce rigid green pellet before sintering. A small amount of binder such as polyvinyl alcohol (PVA) and polyvinyl butyral (PVB) were commonly used to overcome this problem (Cheng et al. 2014; Wei et al. 2015). However, poorly controlled evaporation of binder during sintering resulted in formation of pores in the sample. Although higher temperature and longer sintering duration may enhance atomic diffusion and thus promote densification, the alkaline elements were susceptible to sublimation and hence affect the stoichiometry of the final products (Matsubara et al. 2005). In addition, the commonly used dry powder mixing process in the SSR may produce less homogenous mixture as well as localised chemical variation. On the other hand, wet chemical method such as sol-gel, offer homogenous chemical mixture and wide range of particle size (from nm to μm). Application of different particle size may enhance compactness as well as prevent formation of crack in the pellet during compaction process. Furthermore, due to large surface area over volume, fine powders will promote faster diffusion process and improve the densification during sintering.

The poling process is also crucial for piezoelectric materials. In this process, the material is exposed to a strong external electric field, typically greater than the coercive field, E_c of the material. Although it is necessary to pole the sample to achieve better properties, nevertheless the poling process is frequently associated with the structural orientation particularly at (002) and (200) reflections (Guo et al. 2013; Rubio-Marcos et al. 2010b; Zhao et al. 2012).

In this paper, we report the synthesis of KNN using modified sol gel method with the main objective to study the effect of crystal structure orientation on impedance and piezoelectric properties of the sample. The orientation was achieved via poling process by applying potential difference normal to the surface of the sample. Although the sol had been used to form a KNN film but in this study the process was modified in which the sol was dried and heated to form the KNN ceramic (Li et al. 2012).

EXPERIMENTAL DETAILS

KNN powder has been prepared using sol-gel method (Izzuddin et al. 2014). The starting materials used in this work were kalium acetate (CH_3COOK), natrium acetate (CH_3COONa), lithium acetate (CH_3COOLi) and niobium ethoxide ($\text{Nb}(\text{OC}_2\text{H}_5)_3$) while 2-methoxyethanol and

deionized water were used as the solvents. Initially, 1.25M K^+ and 0.83M Na^+ stocks were prepared by dissolving CH_3COOK , CH_3COONa and CH_3COOLi in 2-methoxyethanol. Based on stoichiometric equation, appropriate amounts of K^+ and Na^+ stock were mixed together for 5 min followed by addition of glacial acetic acid. Prior to $\text{Nb}(\text{OC}_2\text{H}_5)_3$ addition, acetyl acetone was added into the solution to act as a stabilizer which turned the clear solution into yellowish colour. Under N_2 rich ambient, $\text{Nb}(\text{OC}_2\text{H}_5)_3$ was dropped wisely into the solution. Lastly, deionized water was added for hydrolysis process. Preceded with another 1 h stirring process for homogenisation, the prepared KNN sols were then subsequently dried at 200°C for 18 h to form a xerogel.

The xerogel was heated at 800°C for 1.5 h with heating rate fixed at $2^\circ\text{C}/\text{min}$. The produced aggregates were crushed into powder by manual grinding using mortar and pestle for 1 h and then uniaxially pressed at 57 MPa to form a 13 mm diameter pellet. Finally, the pellet was sintered in air for 6 h at 1000°C with $2^\circ\text{C}/\text{min}$ heating rate. The pellet was poled by applying a DC field of 4.0 kV/mm normal to the surface in a silicon oil bath at 100°C for 30 min.

The pellets were characterized using Bruker D8 Advance X-Ray Diffractometers (XRD) and Bruker RFS 100/S Raman spectrometer to obtain the crystallographic information. Microstructure of the synthesized powder and the sintered pellets were evaluated from scanning electron microscope (Zeiss-Supra 55VP VPSEM). For impedance measurement, both surface of the pellets were polished and coated with gold to achieve good electrical contact. The impedance spectrum was recorded using high frequency response analyzer, Solatron 1260 from 100 Hz-10 MHz frequency range with 1000 mV AC-signal at room temperature. The piezoelectric constant, d_{33} of the ceramic was directly measured using quasi-static d_{33} meter (YE2730A, APC International, Ltd). All the characterizations for the poled pellet were conducted after 24 h completion of the poling process. The obtained results were compared between as-sintered and poled pellets.

RESULTS AND DISCUSSION

Figure 1 depicts SEM micrograph of the ceramics after heated at 800°C and grinding process. The micrograph showed the formation of ceramic powder having different morphologies and sizes. There are large particles with right angles which are in μm size regime. The close-up view (inset picture) showed the existence of irregular fine particles ranged from nano to submicron size confirming the formation of ceramics with bimodal particle sizes. However, the nanosize particles cannot clearly be seen from the SEM micrograph. Thus, the determination of finer grains diameter had been done and was tabulated in the histogram (Figure 1(b)) as evidenced of nanoparticles occurrence in the powder.

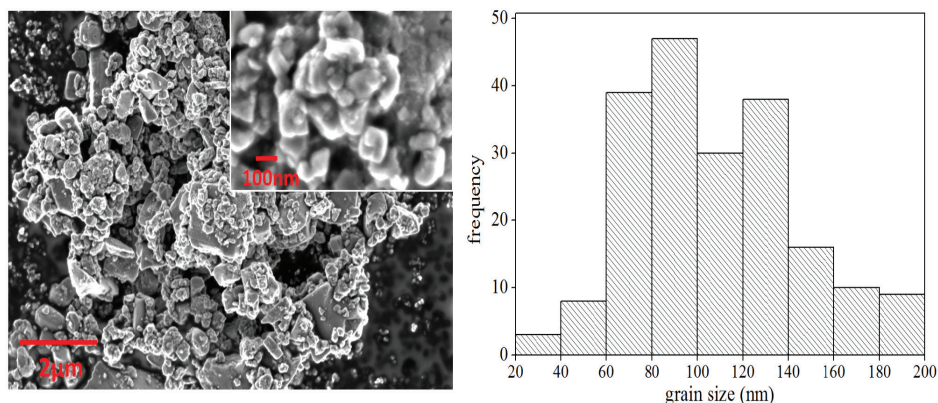


FIGURE 1. (a) SEM image for KNN powders and (b) Histogram of finer grains diameter calculation

The cuboidal grains of different dimensions with $\sim 90^\circ$ edges angle was obtained after sintering process (Figure 2). The formation of larger grains (15 - 20 μm) could possibly be due to the integration of few larger particles after heating process while smaller grains (less than 10 μm in size) formed from the merging of nano-sized particles. The grain growth stops once the particle impinged each other leaving a clean contact between the particles. The absence of intergranular grain boundary signified that the whole process occurred in solid state phase following the Fick's diffusion law. The existence of small number of pores in the sample is related to the retarded grain growth due to limited driving force consequence of inadequate energy, insufficient of particles to be consumed as well as the cuboidal morphology. Nevertheless, it is worth to note the successful compaction procedures employed in this work without the presence of binder. During compaction powder into pellet process, the nano-sized particles filled up the space between larger particles, reduced the pores in the green pellet and improved the contact between particles. Despite using lower sintering temperature compared to earlier report, the sintered pellet exhibited relatively fair density (Safari & Akdogan 2008). Consequently, the poling process was succeeded without any voltage breakdown.

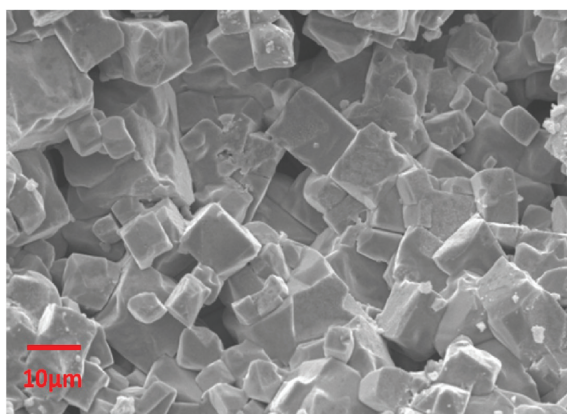


FIGURE 2. SEM micrograph for KNN pellet surface

The X-ray diffractogram for the pellet was illustrated in Figure 3. In general, all peaks can be clustered into six groups which were indexed according to JCPD reference file (00-061-0315). The sample was confirmed as pure $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ existing in monoclinic crystal structure with Pm(6) space group. Based on Pawley method, detail X-ray diffractogram analysis using Diffrac^{plus} TOPAS version 4.2 software showed that the values of KNN lattices parameter are $a = 4.0042 \text{ \AA}$, $b = 3.943 \text{ \AA}$, $c = 3.999 \text{ \AA}$, $\beta = 90.336^\circ$.

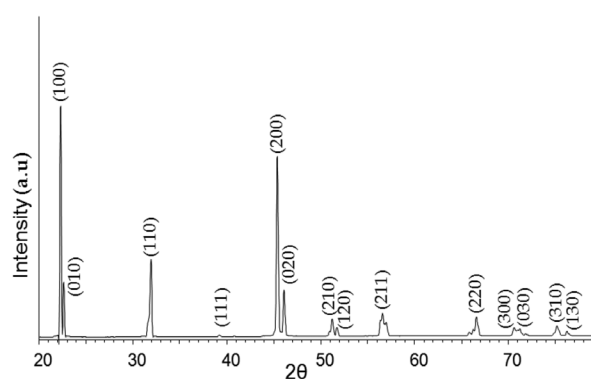


FIGURE 3. XRD spectrum for KNN pellet

Vegard's law is a method to determine the composition of the elements in materials by utilising XRD data (Denton & Ashcroft 1991). It involves the development of calibration line using the reference values certified by ICDD. In this work, a calibration line using K which is heavier and thermally more stable than Na was developed from 11 certified ICDD files. A linear graph with equation $a = 0.0731K + 3.9679$ was obtained. Based on this graph, it was found that the K composition in the ceramics is equal to 0.5 when $a_{exp} = 4.004 \text{ \AA}$, confirming the formation of $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (Figure 4). Simultaneously, this information proves that synthesized KNN has ABO_3 chemical formula which is general chemical formula for perovskite structure.

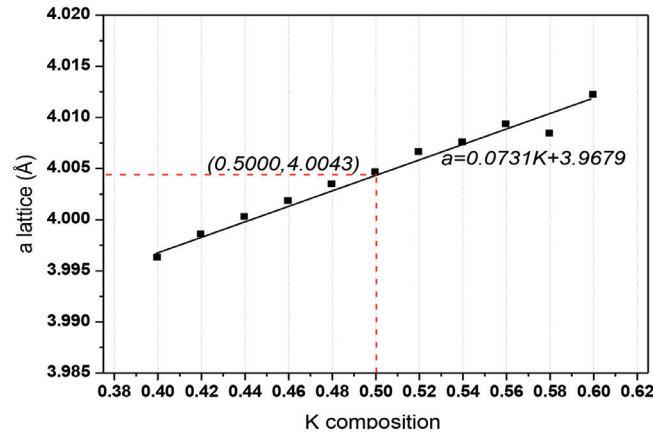


FIGURE 4. Vegards law graph

The X-ray diffractogram after polling process is presented in Figure 5. Obviously, there were dramatic changes in the intensity of the reflection peaks. Although the peak positions remain unchanged, the modification in the reflection intensity suggested that crystal structure re-orientation took place during the poling process and changed the dominant domain from (100) to (110) direction. Detail calculation showed that the percentage ratio for 100: 110 peaks dramatically decreased from 87 to 24% after polarization.

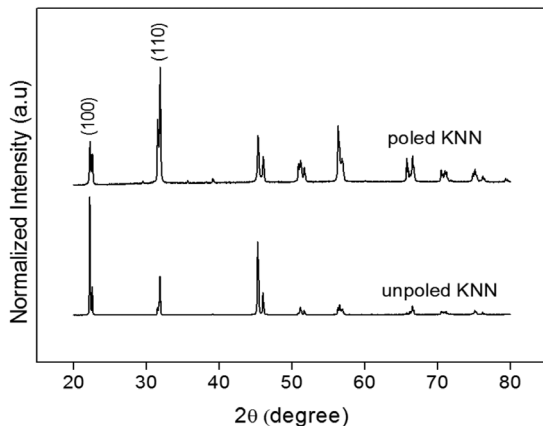


FIGURE 5. XRD spectrum for unpoled and poled sample

The synthesized KNN exhibited responsive internal vibration modes for NbO_6 octahedral as observed from Raman active spectra (Figure 6). The NbO_6 octahedral structure which consists of bending modes at lower frequency and stretching modes at higher frequency confirmed the existence of perovskite structure for the prepared KNN (Rubio-Marcos et al. 2010c). KNN monoclinic structure has three possible space group namely $P2$, $P2/m$ and Pm , but only the latter has Raman active modes (McConnell et al. 1976). This observation was in good agreement with the XRD result. Moreover, this observation signified that the KNN ceramics produced in

this work was sensitive to deformation, a prerequisite for a good piezoelectric material. It was worth to highlight that the absence of any significant modification of Raman spectra after the structural orientation suggested no energy variation required for the deformation.

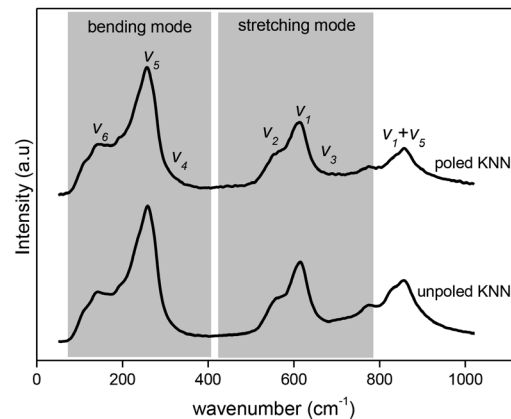


FIGURE 6. Raman spectrum for KNN pellet

Figure 7 shows the Nyquist impedance plot of KNN pellet composed of a single semicircular arc for the unpoled sample. After poling, the sample exhibits a change of the impedance plot due to the new crystal orientation. A combination of depressed semicircular arc and the beginning of another bigger arc at low frequency can be observed. The arc at lower frequency indicates the charge diffusion transfer phenomenon between the electrode-sample interfaces that might occurs after the poling process (Liu et al. 2008; Schmidt et al. 2007).

The semicircle arc can be modeled in terms of an equivalent electrical circuit attributed by the bulk or grains that correspond to a parallel combination of resistor, R_p and capacitor, C_p . Impedance for the parallel RC circuit for perfect semicircle is given by:

$$Z^* = \frac{R_p}{1 + (\omega C_p R_p)^2} - j \frac{\omega C_p R_p^2}{1 + (\omega C_p R_p)^2}$$

The R, C and relaxation time, τ value can be determined from the impedance plot where at the peak of the semicircle:

$$\omega RC = \omega\tau = 1, \quad \omega = 2\pi f_p,$$

where f_p is the frequency at the peak

For the depressed semicircle the equivalent circuit contains combination of a parallel resistor, R and complex capacitor, C^* . According to Jonscher (1983) power law, $C^* = A(j\omega)^{n-1}$. In order to obtain the R and C values, the arc was fitted using:

$$Z^* = \frac{1}{Y^*}$$

$$Y^* = \frac{1}{R} \left[1 + \left(\frac{f}{f_p} \right)^n \cos \frac{n\pi}{2} \right] + \frac{j}{R} \left[1 + \left(\frac{f}{f_p} \right)^n \sin \frac{n\pi}{2} \right] \text{ with } n \leq 1,$$

while the spike area which contains imperfect capacitor the equivalent circuit can also be written as:

$$C^* = A\omega^n \left(\cos \frac{n\pi}{2} + j \sin \frac{n\pi}{2} \right).$$

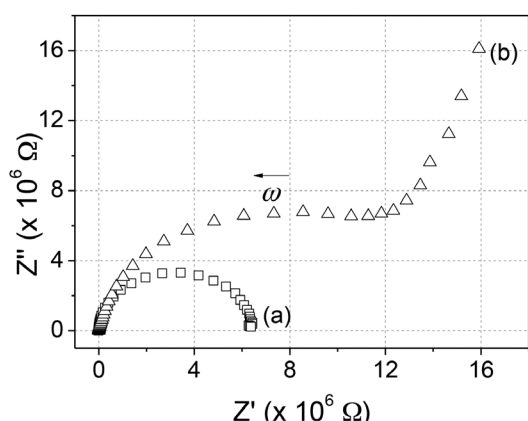


FIGURE 7. Nyquist plot of (a) (100) and (b) (110) structure orientation of KNN

The (100) orientation structure consist of a single conductivity process because it has single semicircular arc (Kim et al. 2009). Besides that, this sample followed Debye-type relaxation process because the arc lie below the real axis (Prasad et al. 2010). Hence, the R and C of the sample could be estimated using instant fit from Z-view software. The value for R and C are $6.4 \times 10^6 \Omega$ and $4.6 \times 10^{-12} \text{F}$, respectively. In contrast, the depressed semicircular arc of (110) orientation structure indicates the sample followed by polydispersive multi-Debye type relaxation or in other words the value of n range in $0 \leq n \leq 1$ (Kim et al. 2009).

The real, Z' impedance versus frequency, f plots of the KNN sample is shown in Figure 8. The sample with

(100) orientation structure comprise of two frequency independent region at low and high frequency with a dispersive region between them. However, the plateau at low frequency diminished after the structured re-oriented to (110) direction. The plateau region is related to the frequency invariant (DC) electrical property of the material. It can be noticed that Z' magnitude is higher at low frequency after the poling process. These properties maybe attributed to the decreasing of ac conductivity in the material due to interfacial polarization effect.

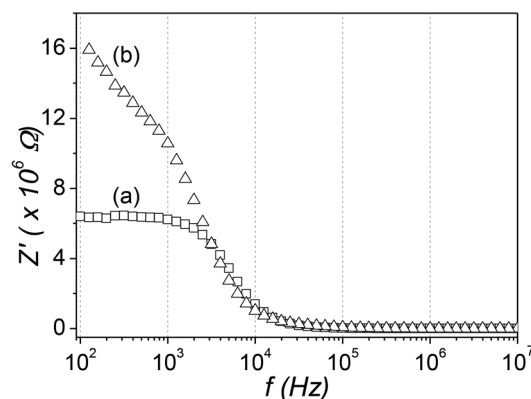


FIGURE 8. Cole-cole plot of Z' vs frequency, f for (a) (100) and (b) (110) structure orientation of KNN pellet

The imaginary, Z'' impedance versus frequency, f plots of the KNN sample is shown in Figure 9. Frequency of relaxation time, τ represent at the peak of Z'' vs f graph. The relaxation time, τ of the material specifies the semicircle position of the prepared KNN through the frequency applied. After structural re-orientation, the relaxation time is shifted to lower frequency.

Generally, there are two main contributing factors to achieve high d_{33} value namely crystal structure and bulk density. Suitable crystal structure is the most important factor because it will specify the net polarization (i.e. domain orientation) of the materials. Materials with

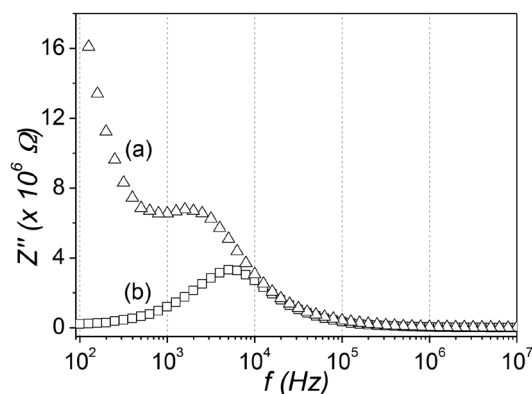


FIGURE 9. Cole-cole plot of Z'' vs frequency, f for (a) (100) and (b) (110) structure orientation of KNN pellet

tetragonal crystal structure is favoured due to high d_{33} resulted from net polarization along (001) direction. After structural re-orientation, d_{33} value for the prepared KNN surged from 5 to 35 pC/N ($\pm 5\%$ accuracy) which was compatible with the previous report (Dolhen et al. 2015). Unlike conventional SSR method, the current work proved that the synthesized KNN via sol gel method stabilized in one of the lowest symmetry crystal namely monoclinic. After the poling process, the monoclinic structure remained unchanged and the crystal re-orientation according to the poling direction was observed which explained the d_{33} value obtained in this work. Moreover, Safari and Akdogan (2008) reported that as the less symmetry structure, monoclinic has up to 24 possible competing polarization directions which further complicate the condition. Furthermore, the presence of even a small percentage of pores was detrimental to the d_{33} of the sample. Utilization of hot isostatic pressing, high energy attrition milling or introducing of dopants into the KNN based has been applied to increase sample density signifying the importance of elimination of pores from the sample to attain better d_{33} value (Safari & Akdogan 2008).

CONCLUSION

The modified sol gel method can be used to prepare KNN powder with different particle size distributions. The presence of bimodal particles improve the packing of the green body and thus facilitates the sintering process. Despite lower sintering temperature, the prepared samples were fairly dense suitable for poling process. The re-orientation of the crystal was observed to significantly alter the impedance behaviour of the material particularly at lower frequency. Despite unfavourable crystal structure, the re-orientation of the monoclinic crystal along (110) direction improved d_{33} value of the sample.

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