CHAPTER 7

Electrical Properties of Potassium Sodium Niobate/Mullite Ceramic Composites

Ceramic composites of potassium sodium niobate (KNN) based on mullite were fabricated via a solid state reaction technique. KNN powder was calcined at 900 °C, and mullite powders were prepared from kaolinite (Ranong, Thailand) and calcined at 1300 °C. The effects of KNN content on the composites properties were investigated, including densification and electrical properties such as dielectric, ferroelectric, and piezoelectric properties. From the resulting data, it was found that the densification can be improved by the addition of KNN. Moreover, the KNN can improve the electrical properties such as remanent polarization, dielectric constant, and piezoelectric coefficient of the materials.

7.1 Introduction

Mullite is a compound of alumina and silica which has the simple chemical formula $3Al_2O_3{\cdot}2SiO_2$. It only rarely originates as a natural mineral. Generally, mullite can be prepared from various alumina and silica by various techniques such as sol-gel, precipitation, hydrothermal, and chemical vapor deposition [1-2]. Furthermore, mullite can be prepared from kaolin clays. The main phase after firing kaolin at high temperature is mullite [3]. Nowadays, mullite is one of the most important candidate materials for creating traditional advanced ceramics. It is widely used as a structural and functional ceramic, such as in reinforced composites [4], microelectronic packaging [4], electrical insulation substrates [4] and thermal components [5]. Since mullite has many benefits which include resistance to high thermal shock [6], high thermal conductivity [6], low dielectric constant ($\varepsilon_r \sim 6$ - 7 at 1 kHz), creep resistance [6-7], temperature stability, and good chemical inertia [6, 8-9], the work for improving the properties of mullite is of continuing importance.

In recent years, lead free ceramics have been intensively studied due to the environmental concern. Among various lead-free candidates, potassium sodium niobate ($K_{1-x}Na_xNbO_3$ or KNN) has been considered one of the most promising alternatives because of its high Curie temperature and good ferroelectric and piezoelectric properties [10]. KNN is a combination between ferroelectrics $KNbO_3$ (KN) and anti-ferroelectrics $NaNbO_3$ (NN), reported to have high piezoelectric properties near the morphology phase boundary or MPB when $x = 0.5$ [11]. KN ceramic with ferroelectric orthorhombic symmetry at room temperature has phase transitions similar to $BaTiO_3$ but with higher T_c (~ 420 °C). NN ceramic is an orthorhombic anti-ferroelectric at room temperature with T_c = 355 °C [12-13]. This material has been widely studied due to its high transition temperature, high remnant polarization, and high radial coupling coefficients. Therefore, this material has been proposed for use in many electronic applications such as piezoelectric actuators, sensors and transducers [14-17]. However, it is very difficult to obtain dense and well sintered KNN ceramics using an ordinary sintering process [14] and rapid-rate sintering [18] because of the high volatility of alkaline elements at high temperatures [10]. Moreover, the KNN phase is not stable at high temperature (> 1140 °C for potassium niobate) [14]. One technique to prepare dense ceramics and fine microstructures is two step sintering (TSS) [19]. In the first step of TSS, the sample is heated to high temperature (T_1) for a short time to achieve a critical density. Then the sample is cooled to a lower temperature (T_2) and soaked the time at T_2 for densification without gain growth (second step). This method can help to improve many properties of lead free ceramics [20].

Recently, many studies have focused on composites of clays and piezoelectric materials such as kaolinite-$BaTiO_3$ [21-22], kaolinite-$SrTiO_3$ [23], and mullite- $Ba(Zr_{0.07}Ti_{0.93})O_3$ [24]. The electrical properties of these composites were found to improve by the addition of piezoelectric phases. To our knowledge, the properties for composites of mullite and KNN ceramics have not been investigated. In the present work, ceramic composites of mullite and KNN were therefore fabricated. Mullite-based ceramics were synthesized from kaolin clay at high temperature, and the composite ceramic was sintered using the two step sintering method. KNN powder was fabricated using a convention mixed oxide method. Physical properties, phase evolution and electrical properties, *i.e.* the dielectric, ferroelectric and piezoelectric properties of the composite samples, were investigated and discussed in details.

7.2 Experimental

The starting materials of the composite are kaolinite clays (Ranong, Thailand), Na_2CO_3 (99.5%, Sigma-Aldrich), K_2CO_3 (99%, Sigma-Aldrich) and Nb_2O_5 (99.95%, Cerac) powders. The mullite powder was synthesized by firing kaolinite clays at 1300 °C for 2 h. The potassium sodium niobate with formula $K_{0.5}Na_{0.5}NbO_3$, or KNN powder, was prepared by the conventional mixed oxide method. The starting powders were mixed by ball milling in an ethanol medium for 24 h, then dried in an oven at 110 °C for 24 h, and then calcined at 900 °C for 5 h. The KNN powders were mixed with a polyvinyl alcohol (PVA) binder, then formed into pellets using uniaxial pressing, and then sintered using the two step sintering method (TSS) with T_1 = 1150 °C and T_2 = 1050 for 2 h [19]. After that, the obtained KNN ceramic was crushed and then sieved into pieces less than 0.5 mm. The ceramic composites were mixed by combining the mullite powder and KNN fragment ceramic in the ratios of 0, 20, 40, 60, 80 and 100 vol%, and then ball milled in ethanol for 10 h. After that the mixed powder was combined with PVA binder and then formed into pellets. Next, the green pellets were sintered using the TSS method with T_1 = 1000 - 1600 °C and T_2 = 900 - 1500 °C for 2 h.

The bulk density of all sintered ceramic was measured using the Archimedes method. Phase formation was identified using the X-ray diffraction technique (XRD) with CuKα radiation (Philips, X'Pert-MPD). For electrical measurement, the samples were polished to ~1 mm thickness, painted with silver on both sides, and then heated at 500 °C for 0.3 h. The dielectric properties at different temperatures were measured by using an LCR meter (Model E4980A, Agilent Technologies) connected to the furnace, which controlled the temperature in a range of 25- 450°C with frequencies ranging from 100 - 1000 kHz. The ferroelectric properties were measured via a standard ferroelectric analyzer (Radiant with Trek model 609B Precision High Voltage Interface). An AC electric field of 20 kV/cm and a frequency of 1 Hz were used in the *P-E* measurements. The piezoelectric coefficient (d_{33}) of the composites was measured using a d_{33} meter (KCF technologies, model S5865), after poling the samples in a silicon oil bath by applying an electric field at 2 kV/mm for 30 min.

7.3 Results and Discussion

The optimum density of the ceramic composite for different sintering temperatures (1000-1600 °C) was shown in Fig. 7.1. Optimum density was selected for study due to ceramic with high density often having good properties. It was found that the amount of KNN impacted the optimum sintering temperature, which decreased as the amount of KNN increased. It can be concluded that the amount of KNN affected the sinterability of the studied composites [22]. This may be because KNN has an optimum sintering temperature around ~ 1100 - 1120 °C, which is lower than that of the mullite (~ 1600 °C) [25]. Moreover, the ceramic composites have new phases such as potassium aluminum silicate when sintering temperatures are lower (e.g. ~ 1100 °C for potassium aluminum silicate). The new phases may be caused by the reaction between mullite and KNN during sintering [26]. It should be noted that new phases have also been observed in other mullite based composites [21-22].

Bulk density, as a function of the KNN content of mullite/KNN ceramic composites at optimum sintering temperatures, is shown in Fig. 7.2. The measured density increased as the amount of KNN content increased. KNN can improve the density of the ceramic composite because KNN has a higher density value than mullite. Normally, the density of composite (ρ_c) can be calculated using the equation:

$$\rho_c = \sum_{i=1}^{n} \rho_i V_i \tag{7.1}$$

where ρ_c is density of composites, ρ_i is density of each phase, V_i is volume fraction of each phase and n is number of the phases. In the present work, the density of the mullite/KNN composites can be calculated as follows:

$$\rho_c = \rho_{\mathrm{mullite}}(1\text{-}V_{\mathrm{KNN}}) + \rho_{\mathrm{KNN}} V_{\mathrm{KNN}} \tag{7.2}$$

where ρ_c is the density of the composite (calculated density), ρ_{mullite} is the density of the mullite powder (ρ_{mullite} = 2.52 g/cm^3, obtained from Archimedes method), ρ_{KNN} is the density of the KNN ceramic powder (ρ_{KNN} = 3.61 g/cm^3, obtained from Archimedes method) and V_{KNN} is the volume fraction of KNN. The value of calculated density increased as the amount of KNN content increased. Furthermore, the trend of the calculated density agreed with the measured density. In this work, measured density relates to the volume fraction of KNN, shown as follows: $\rho = 0.0083V_{KNN} + 2.5831$.

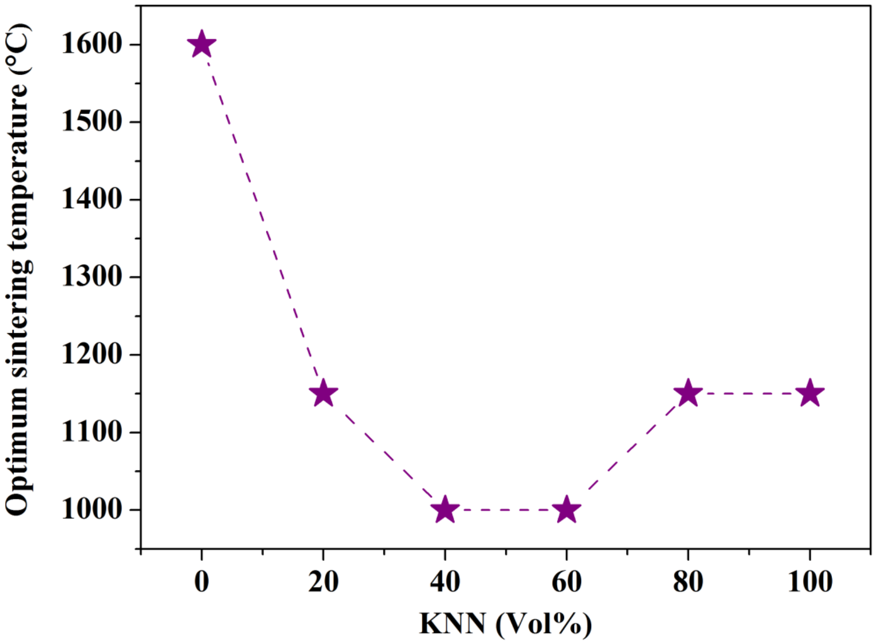

Figure 7.1 Optimum sintering temperature (at T_1) versus KNN content of mullite-KNN samples.

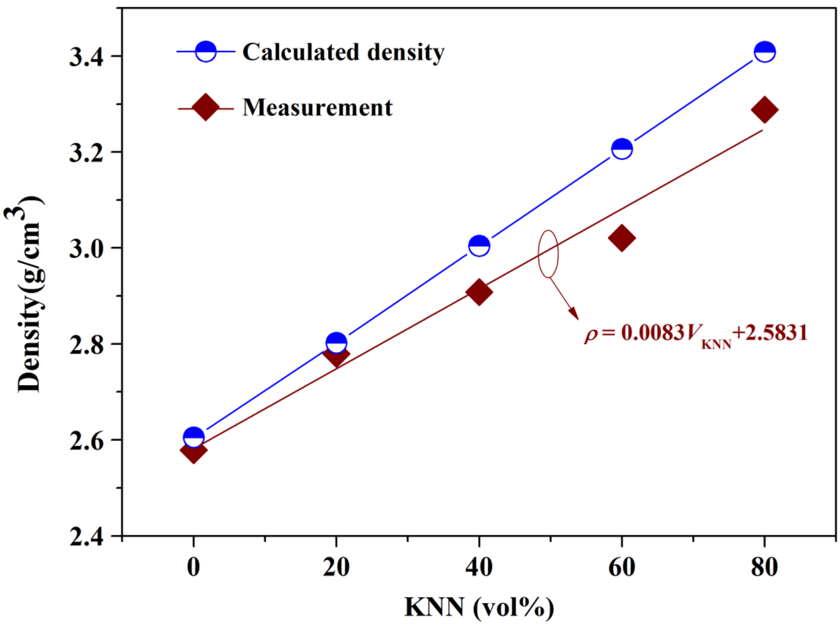

Figure 7.2 Plots of bulk densities as a function of KNN content of mullite-KNN samples.

The XRD patterns of the studied sample are shown in Fig. 7.3. The XRD patterns show the pure phase of the KNN and the mullite phase, which match JCPDS files no. 01-077-0038 and 00-002-0431, respectively. The composite samples exhibited other phases such as sodium potassium niobate ($Na_{0.1}K_{0.9}NbO_3$), potassium niobium oxide ($K_2Nb_8O_{21}$), potassium aluminum silicate (Kalsilite: $KAlSiO_4$), sodium niobium oxide ($NaNb_3O_8$), niobium oxide (Nb_2O_5) and quartz (SiO_2). This may be due to some reaction between mullite and KNN during the sintering process at high temperatures. For example, some parts of $Na_{0.5}K_{0.5}NbO_3$ may react with the mullite, causing multiphase formation [27].

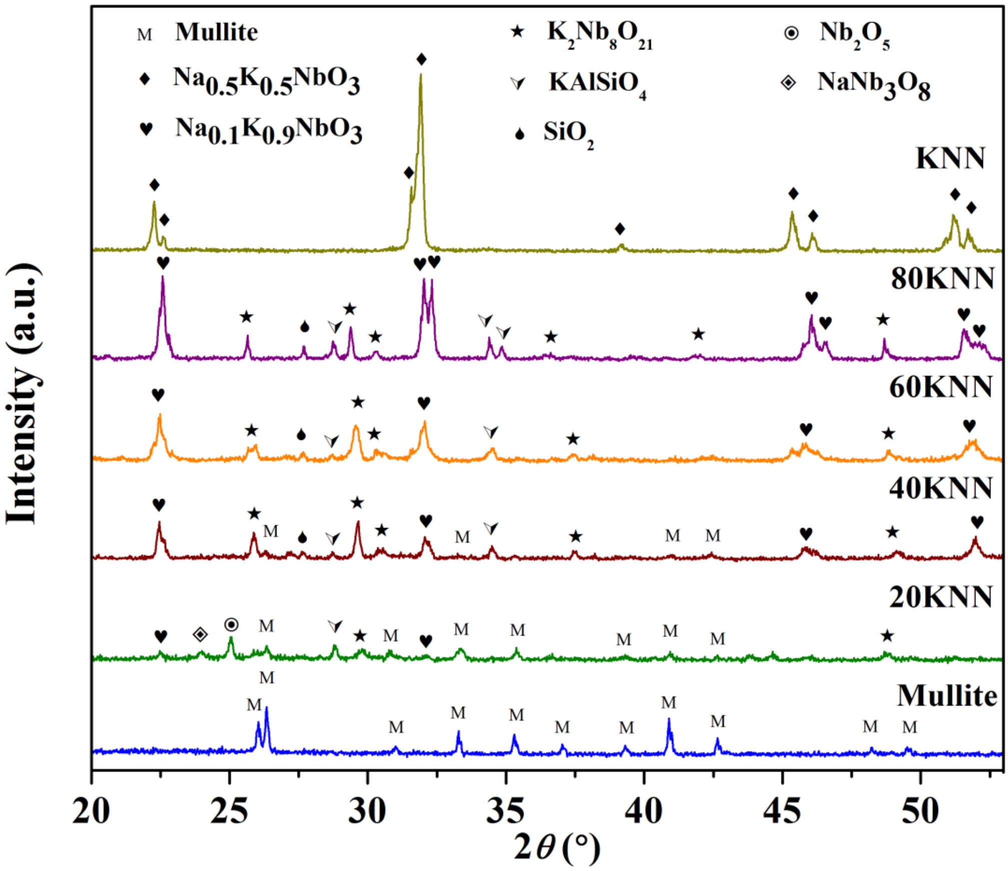

Figure 7.3 XRD patterns of mullite-KNN samples sintered at optimum sintering temperature.

The polarization-electric field (*P-E*) hysteresis loops of the mullite-KNN samples are shown in Fig. 7.4. It was found that the mullite ceramic sample showed non-ferroelectric behavior: a very slim and slant hysteresis loop for this sample indicated a type of non-conductor. With KNN added, the hysteresis loop transformed to be a ferroelectric hysteresis loop. This indicates that the KNN additive induced ferroelectric behavior in the sample. The P_r value versus KNN content is shown in Fig. 7.5. The P_r value increased with increasing KNN content. The ferroelectric properties of the composite could have improved due to the KNN producing higher total polarization in the samples [21].

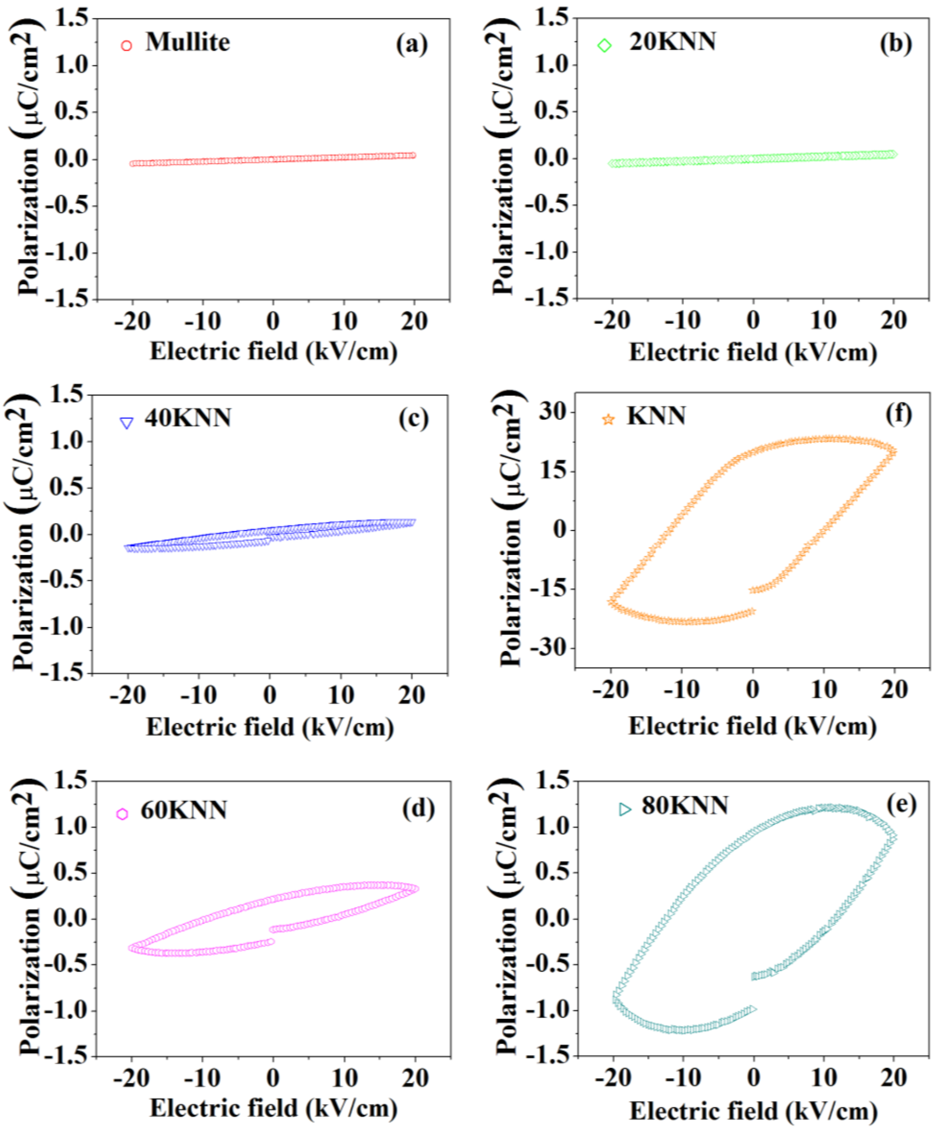

Figure 7.4 *P-E* hysteresis loops of the mullite-KNN samples sintered at optimum sintering temperature, measured under an electric field of 20 kV/cm and a frequency of 1 Hz where (a) mullite, (b) 20 vol% KNN, (c) 40 vol% KNN, (d) 60 vol% KNN (e) 80 vol% KNN and (f) KNN.

The piezoelectric coefficient (d_{33}) of the studied samples is shown in Fig. 7.5. The d_{33} value of the samples increased with the amount of KNN. It was found that the d_{33} value trend is similar to the trend of the P_r. Generally, from the theory of piezoelectricity, d_{33} has a relation with the d_{33} value which can be shown as follows:

$$d_{33} = 2\varepsilon_{33}\varepsilon_0 Q_{11} P_r \tag{7.3}$$

where ε_{33} represents the dielectric constant of the material and ε_0 is the vacuum permittivity, and Q_{11} represents the electrostrictive coefficient, which is a constant for perovskite materials. Therefore, the reason for the improvement of the d_{33} value should be linked with the increase of the P_r value.

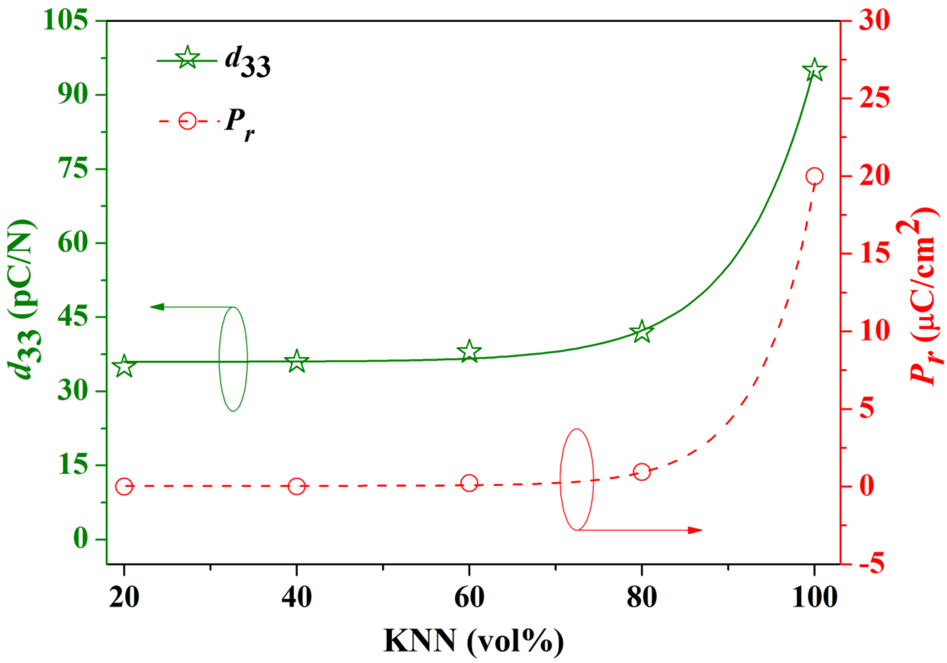

Figure 7.5 Plots of piezoelectric coefficient (d_{33}) and remnant polarization (P_r) value as a function of KNN content of mullite-KNN samples.

The dielectric constant (ε_r) and dielectric loss ($tan\delta$) as a function of frequency at room temperature are shown in Fig. 7.6. For all measurement frequencies, the dielectric constants increased as the amount of KNN increased. This corresponded with the higher total polarization which occurred as additive concentration increased [28]. At high frequency regions, mullite and all composites showed high dielectric stability. Low frequency regions had a high of ε_r. This may be due to the effects of polarization (*i.e.* atomic, ionic, dipolar and space charge polarization). However, with an increase in frequency, some of these contributions lagged behind, not following the field variation and becoming inactive. At high frequencies, all the other modes of polarization faded away and electronic polarization became the dominant mode of polarization; therefore, ε_r decreased at high frequencies [29]. Dielectric loss of all samples also slightly decreased as frequency increased, except for the mullite, KNN and 20vol% samples (Fig. 7.6).

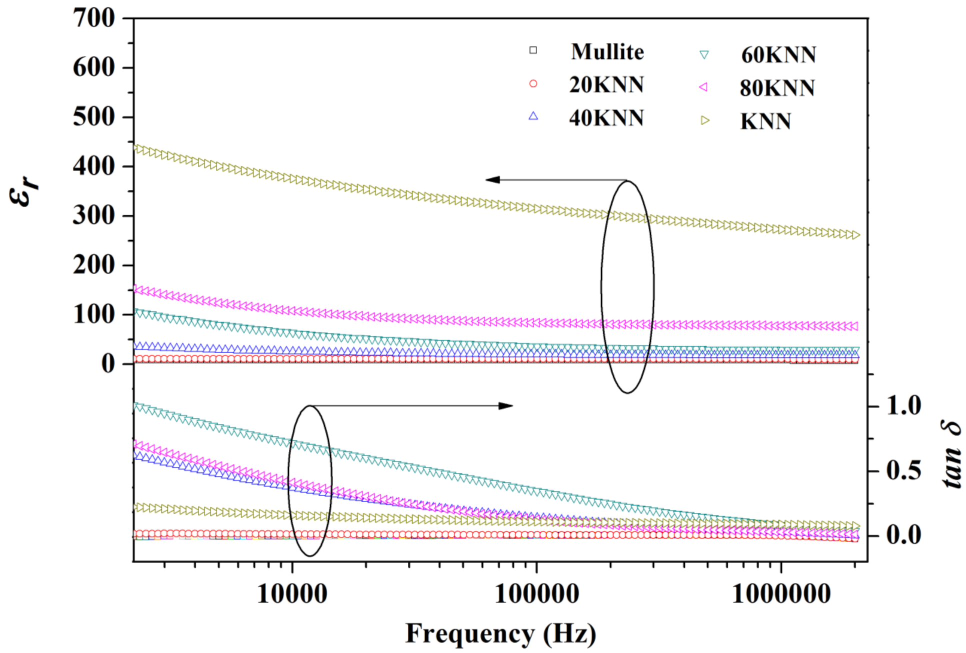

Figure 7.6 Plots of dielectric constant (ε_r) and dielectric loss ($tan\delta$) of mullite-KNN samples (at room temperature) as a function of frequency.

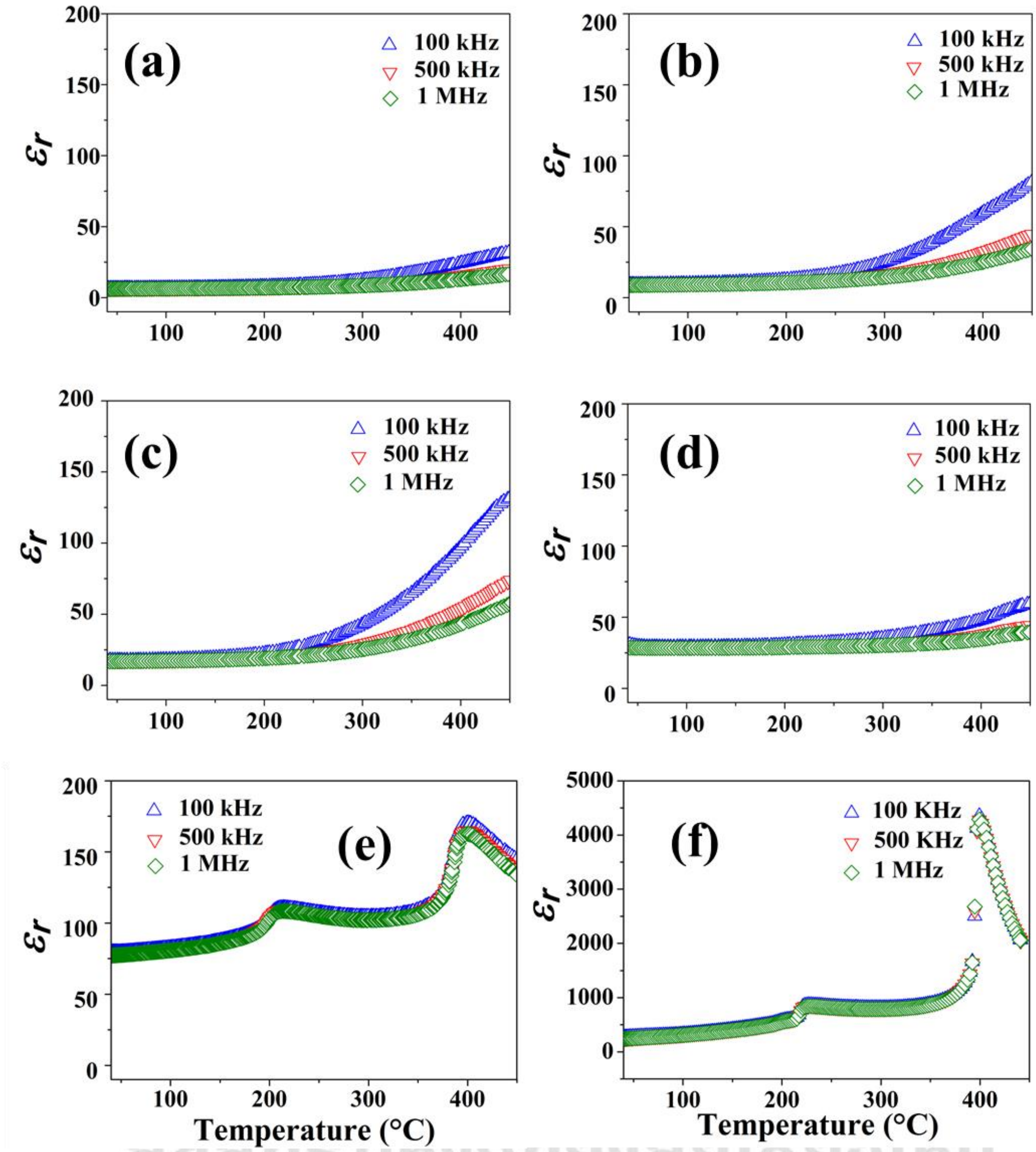

Figure 7.7 Temperature dependence of dielectric constant for the mullite-KNN samples, measured at various frequencies from 100 - 1000 kHz where (a) mullite, (b) 20 vol% KNN, (c) 40 vol% KNN, (d) 60 vol% KNN (e) 80 vol% KNN and (f) KNN.

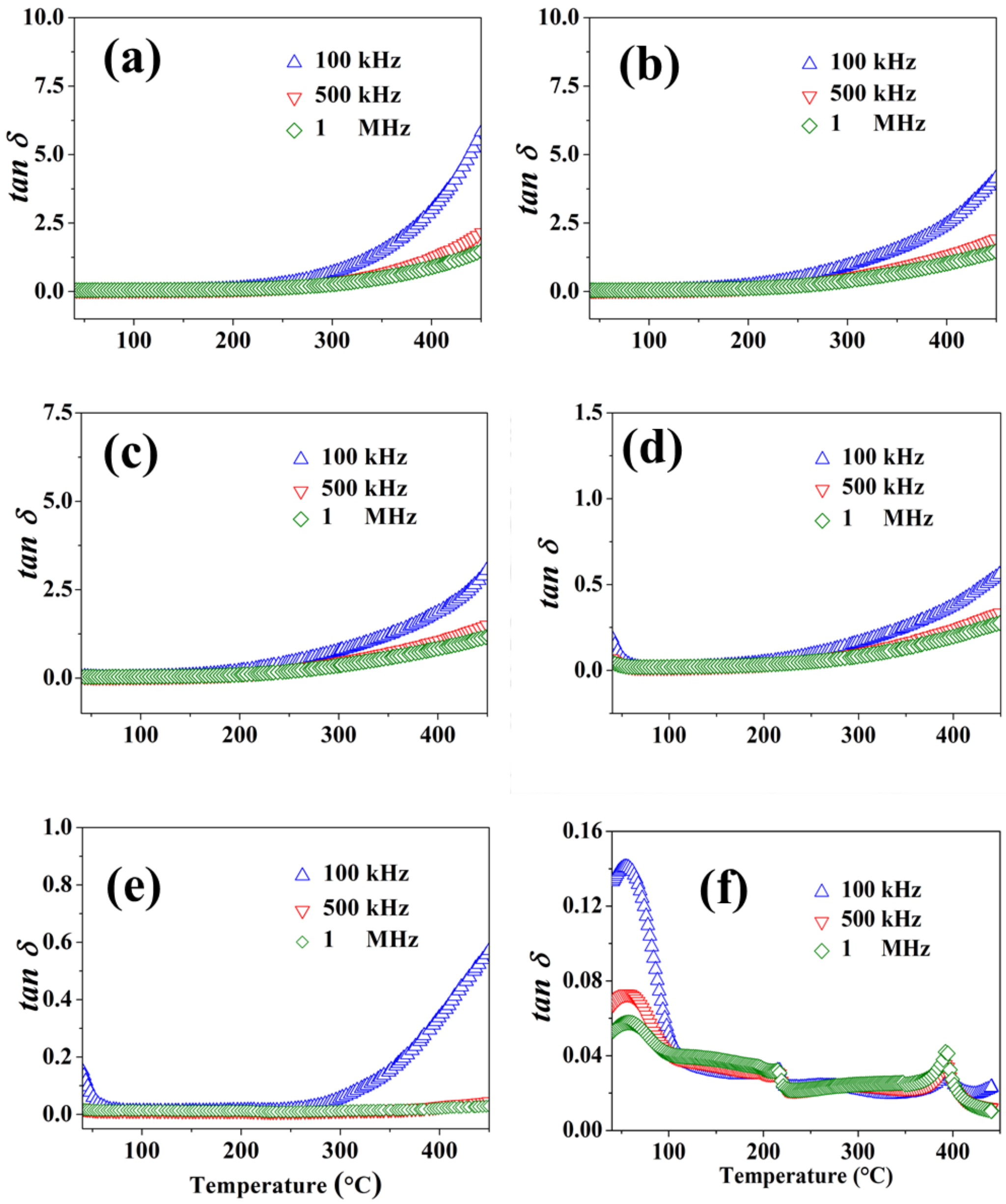

Figure 7.8 Temperature dependence of dielectric loss for the mullite-KNN samples, measured at various frequencies from 100 - 1000 kHz where (a) mullite, (b) 20 vol% KNN, (c) 40 vol% KNN, (d) 60 vol% KNN (e) 80 vol% KNN and (f) KNN.

Temperature (*T*) dependence of ε_r and $tan\delta$ of the studied samples, measured at various frequencies from 100 - 1000 kHz, is shown in Fig. 7.7 and Fig. 7.8. The dielectric of the samples with KNN less than 80 vol% was stable especially at temperatures < 200°C. However, the dielectric constant increased as the temperature increased (> 200°C). The samples with 80 and 100 vol% of KNN showed two phases with transition temperatures. The transition temperature around 220 °C had an orthorhombic-tetragonal phase transition (T_{orth}-T_{tetra}), while the transition temperature around 400 °C (T_c) had a tetragonal to cubic phase transition [30]. The maximum dielectric constants of the 80 vol% and KNN samples at T_c were 171 and 4,394, respectively. Furthermore, the 80 vol% sample exhibited broad transition peaks. This may be due to the effects of this sample having multiple phases, with each phase having a different dielectric constant which then resulted in broad dielectric constant-temperature curves, having lower dielectric constants than those of the KNN sample. The $tan\delta$ - T curves indicated an improvement of $tan\delta$ especially at high temperature (Fig. 7.7), which may have been due to the KNN ceramic exhibiting low $tan\delta$ at high temperature.

7.4 Conclusion

In this study, ceramic composites of mullite and KNN were successfully synthesized via a solid-state mixed oxide method. The properties of the samples were investigated such as physical properties, phase formation and electrical properties, which varied with KNN-added content. The amount of KNN had an effect on the sintering temperature and phase of the samples. Density increased as KNN content increased. The KNN additive also improved the electrical properties. The improvement of all electrical behavior was a result of the higher amount of piezoelectric phase (KNN) producing higher total polarization in the samples.

7.5 Reference

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