



# Solvothermal Synthesis, Sintering Behavior and Dielectric Properties of Potassium Niobate Fine Powders

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Received: 22 July 2010

Accepted: 30 December 2010

## ABSTRACT

Fine potassium niobate powders composing of sub-micrometer sized lumber particles were synthesized under solvothermal conditions, with the use of mixed water-ethyl alcohol as the reaction medium and the application of the prior ultrasonication as the activation step. The influences of ethyl alcohol on particle shape and size, and the prior ultrasonication on the sintering behavior of the synthesized powders are present and discussed in relative to the conventional hydrothermal cases. The temperature dependent dielectric constants ( $\epsilon_r$ ) and dielectric losses ( $\tan \delta$ ) of the sintered ceramics are also included, showing the origin of the losses to stem from the loss of potassium oxide in the sintering process.

**Keywords:** potassium niobate, solvothermal synthesis, sonocatalyzation, sintering, dielectric property.

## 1. INTRODUCTION

The emergence of the “*green attitude*” has resulted in the attempts to develop the green alternatives for various technologically important materials and processes including lead, despite of its important role technologically. Along this line, potassium niobate ( $\text{KNbO}_3$ , KN) has appeared as one of potential candidates for the lead-free piezoelectric materials. This is due to its excellent inherent properties and potential applications, for example, as an optical wave guide and devices for frequency doubling, holographic storage and surface acoustic wave [1-5]. The material is conventionally prepared by solid state reactions, which demand high temperatures and multiple cycles of heating-

and-grinding to assure the completeness of the reactions [6]. Besides being the energy-consumable process, the other drawbacks of the solid-state processes such as the formation of undesired impurities and aggregations are inherent [7]. During the last decade, the hydrothermal technique has been proved to be efficient for the preparation of KN in various forms, including fine powder, one-dimensional structure and thin film [8-11]. Despite of the promising future of the material and the technique, the practical application and commercialization of KN yet faces a major problem with sintering. At effective sintering temperature and duration,

the rapid vaporization of potassium oxide ( $K_2O$ ) and the large difference in properties of the cation involved result in the chemical control and densification problems [1]. The additions of other aiding compounds, such as magnesium oxide (MgO) and lead oxide (PbO), were reported to relieve the problems [12, 13].

Here, the adaptation of hydrothermal process by the use of mixed water-ethyl alcohol as reaction medium for the preparation of KN fine powders is described. The application of the ultrasonic wave on the reaction mixtures in prior to the synthesis is discussed. The sintering behavior and the preliminary investigation of the dielectric properties of the sintered ceramics are reported.

## 2. MATERIALS AND METHODS

The mixtures of niobium oxide ( $Nb_2O_5$ , Sigma-Aldrich 99.99%, 0.0056 mol) and potassium hydroxide (KOH, Merck 85%, 0.0028 mol) were first prepared in mixed water-ethyl alcohol liquid medium (0.278 mol of water, 0.086 mol of ethyl alcohol;  $C_2H_5OH$ , Merck 99.9%). The employed amount of KOH functioning as both reagent and mineralizer in the synthesis is the amount reported as the critical limit providing the successful synthesis [14]. Each mixture was then stirred and transferred into Teflon liners up to *ca.* 80% filling volume capacity. The mixtures were subsequently subjected to an autogenous pressure developed at 200°C for 1-24 hours. In order to study the effect of ultrasonication, some samples are ultrasonicated at 40( $\pm$ 5)°C for 1 h using a laboratory ultrasonic bath (Bandelin Electronic RK255H, 160/320W, 35kHz) before the reactions. The synthesized powders were finally recovered by filtration and washed with water until the pH of the filtrate was *ca.* 7 to assure the complete removal of the alkali.

Powder X-ray diffraction (XRD; Bruker

D8 Advance diffractometer, Ni-filtered,  $CuK_\alpha$ ,  $\lambda=1.54098 \text{ \AA}$ , 40 kV, 30 mA) was used in characterizing the synthesized crystalline phases. Lattice parameters of these phases were refined from the collected XRD patterns. Selected area electron diffraction (SAED) equipped by a transmission electron microscope (TEM; JEOL JEM-2010) was also used in characterizing growth direction of the elongated particles, whereas a field emission scanning electron microscope (SEM; JEOL JSM-6335F) was used in examining morphologies and sizes of the composing particles.

The synthesized powders composing of a single orthorhombic KN according to the XRD results were chosen for the sintering experiments. The powders were ground and pressed uniaxially at 100 bars and room temperatures to make the pellets of 10.15 mm in diameter and 2.45-2.75 mm in thickness. The obtained pellets were then sintered at 1,025°C for 1 hour (Carbolite, 2416CG) using a heating-cooling rate of 3°C min<sup>-1</sup>. After the sintering, densities of the sintered ceramics were evaluated using Archimedes technique [15]. Phase and microstructure of the sintered pellets were investigated by XRD and FESEM, respectively.

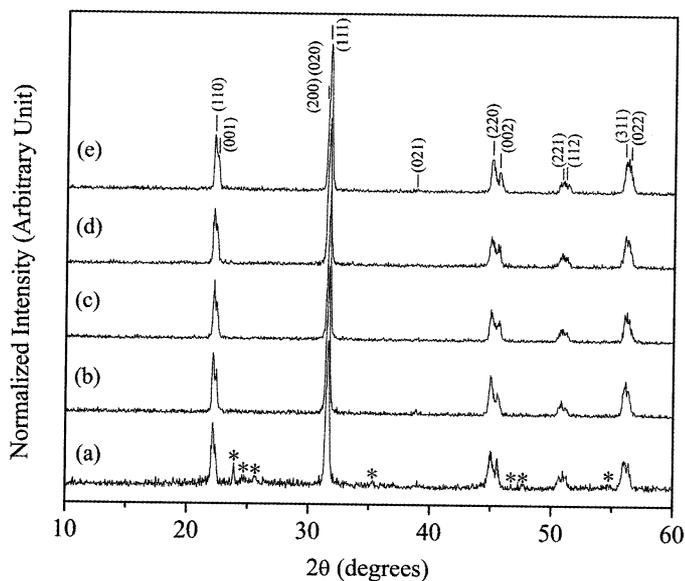
The dielectric properties of the sintered ceramics were studied as functions of both temperature and frequency using an automated dielectric measurement system and a silver electrode (Dupont, QS 171), which was prepared by printing on the lapped surfaces followed by firing at 600°C for 1 h. The computer-controlled dielectric measurement system consists of a precision LCR meter (Thonghui, TH2819A) and a temperature chamber. The temperature dependent measurements were performed using a Keithley Model 2,000-digit multimeter which was equipped by a temperature chamber, when the capacitance and the dielectric loss

tangent were determined over the temperature range of 50-500°C with the frequency ranging from 0.1 to 100 kHz.

### 3. RESULTS AND DISCUSSION

Figure 1 and 2 shows the XRD patterns of the powders obtained from the reactions conducted at 200°C for varied reaction times, with and without prior ultrasonication for an hour, respectively. The application of the ultrasonication as described did not showed any significant difference in the XRD patterns of the synthesized powders. When the reactions were conducted for an hour, the presence of the other diffraction peaks which were not of the desired KN was plain. The identification of these phases could not be precisely done due to a deficiency in number

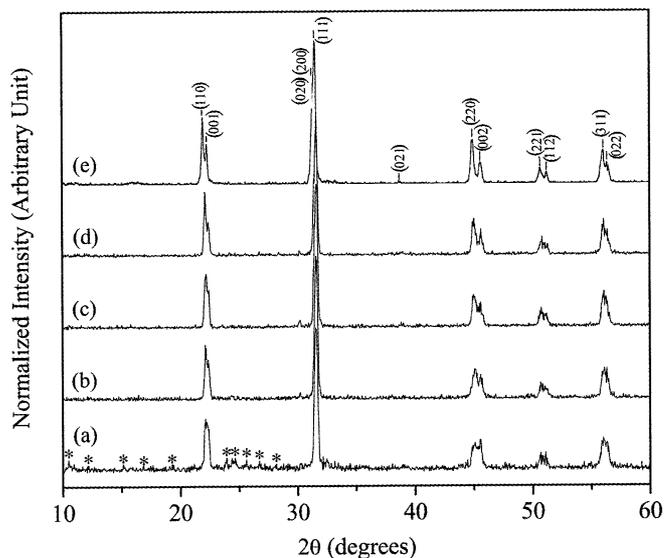
and intensity of these peaks. It can be nonetheless ascertained that the formation of KN, which could be indexed as the orthorhombic phase with space group  $Cm2m$  (JCPDS 32-822), already occurred as the major phase. According to the XRD results, the pure phase of KN could be obtained after 3 h, irrespective to the application of the prior ultrasonication on the reaction mixtures. The obtained KN powders could be readily indexed and refined in orthorhombic  $Cm2m$  (JCPDS 32-822), giving  $a = 5.689(8)$ - $5.695(8)$  Å,  $b = 5.721(11)$ - $5.737(10)$  Å and  $c = 3.982(11)$ - $3.984(12)$  Å. There was not therefore any apparent effect of the ultrasonication on the formation and phase of the synthesized KN powders, within a limit of the XRD technique.



**Figure 1.** The XRD patterns of the powders obtained from the reactions conducted at 200°C for (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h and (e) 24 h on the ultrasonicated mixtures; \* indicates unidentified diffraction.

The SEM images show the synthesized KN powders to compose mostly of lumber particles with a few fraction of pseudo-cubic particles, independent also on the preparative

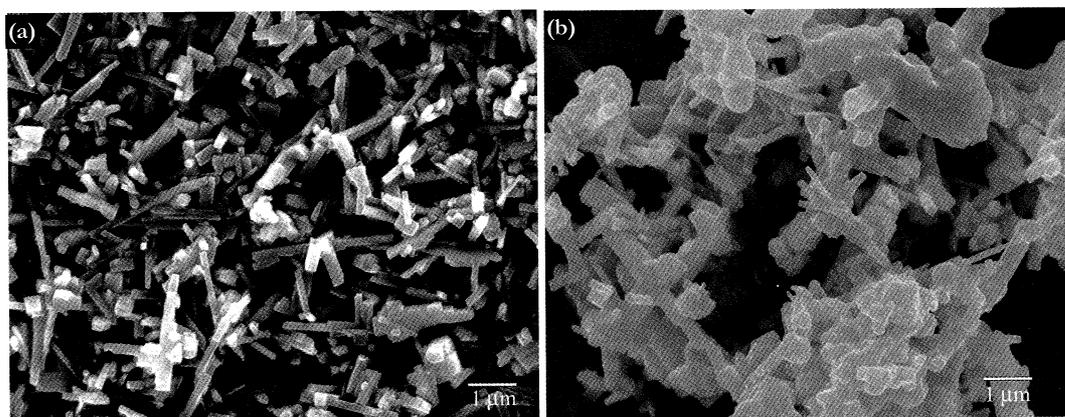
conditions. Figure 3 shows the representative images of the particles obtained from the reactions with and without the prior ultrasonication, illustrating well-defined shape



**Figure 2.** The XRD patterns of the powders obtained from the reactions conducted at 200°C for (a) 1 h, (b) 3 h, (c) 6 h, (d) 12 h and (e) 24 h on the mixtures without the prior ultrasonication; \* indicates unidentified diffraction.

of the KN particles for the powders obtained from the reactions with the prior ultrasonication. Sizes of these KN particles measured directly from the SEM were distributed in a range of approximately 0.1-1  $\mu\text{m}$  and 0.15-2.5  $\mu\text{m}$ , for the short and long axes, respectively. In contrast, the particles with a serious melting and poor-defined particle boundary were obtained from the reactions conducted without the prior application of the ultrasonic

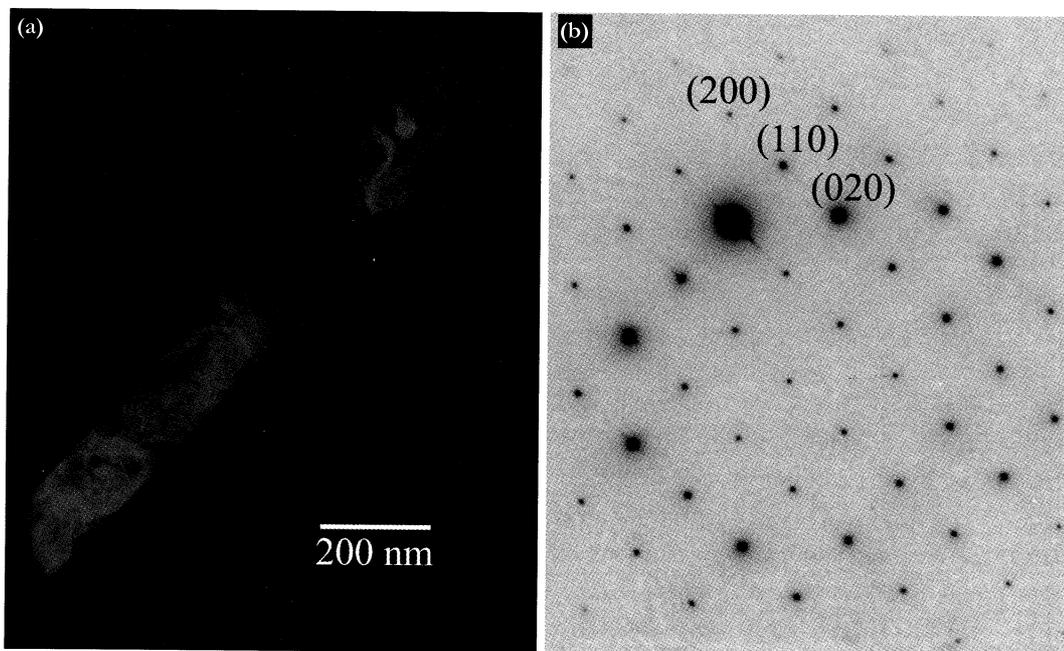
wave. This may be rationalized by the ability of the ultrasonic wave in inducing the nucleation and in creation of the highly reactive and clean surface on the created nuclei which should promote the clean crystal growth in the afterward reactions [16]. The pressure generated under the solvothermal conditions generally causes the nucleation to occur as simultaneously as the crystal growth, which commonly results in hard aggregates [17].



**Figure 3.** The SEM images exemplifying the lumber particles of potassium niobate derived from the reactions on (a) the ultrasonicated reaction mixture and (b) the mixture without prior ultrasonication, conducted under the same synthesis conditions.

In comparison to the former reports on the synthesis of KN fine powders using the hydrothermal reactions at the same temperature and KOH concentration of  $200^{\circ}\text{C}$  and  $8\text{ mol dm}^{-3}$ , several differences could be pointed out, although phase of the obtained KN is the same, which is the orthorhombic phase [14]. First, shape of the hydrothermally derived KN particles was largely pseudocubic, when the lumber particles could be obtained in this study. Second, sizes of the pseudocubic

particles were also distributed in a larger size region of 1-4  $\mu\text{m}$ , compared to the sub-micrometer sizes reported here. The use of mixed water-ethyl alcohol as a liquid medium apparently provided smaller sized and more elongated particles. Regarding the effective reaction, the employment of ethyl alcohol and the application of ultrasonic wave on the reaction mixtures did not result in any significant change.



**Figure 4.** (a) The TEM image of the typical lumber potassium niobate particle with (b) the corresponding indexed SAED pattern based on the orthorhombic  $Cm2m$  (JCPDS 32-822).

The structure of the lumber particles was also evaluated through selected area electron diffraction (SAED) in the transmission electron microscope. Figure 4 shows the TEM images of the typical particle and the corresponding SAED pattern, which could be well indexed in the assigned orthorhombic  $Cm2m$  phase. The growth direction apparently lied along the crystallographic  $[110]$  direction.

The KN powders characterized by the XRD to be of the single orthorhombic phase

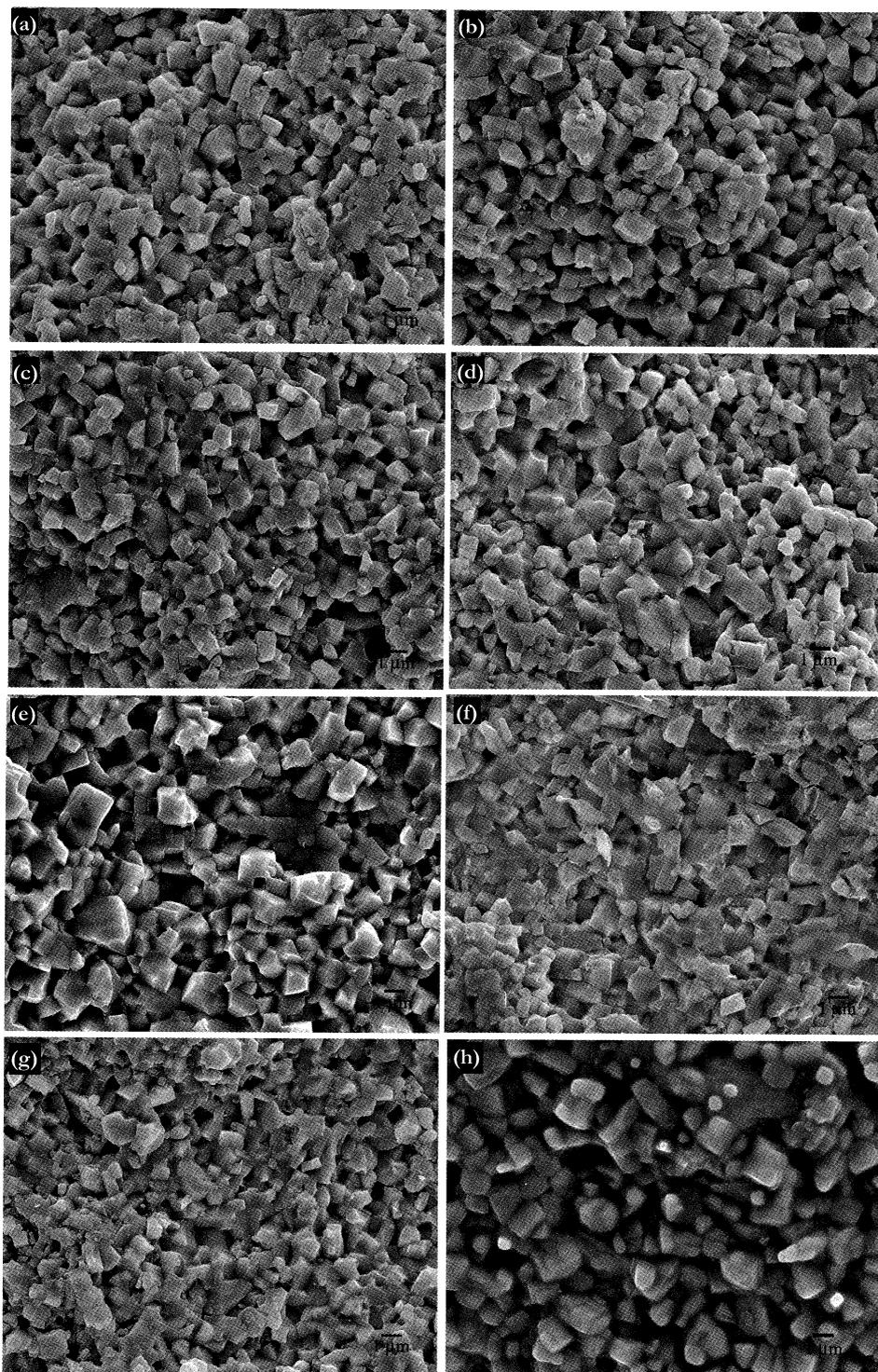
were chosen for the sintering experiments, including those obtained from the reactions conducted for 3-24 h, both with and without the prior ultrasonication. After the sintering, the diameters and thickness of the sintered bodies were substantially reduced; 8.35-8.60 mm and 2.10-2.30 mm for the sintered pellets compared to 10.15 mm and 2.45-2.75 mm for the green bodies. The contraction in diameter of *ca.* 18% was slightly better than the contraction in thickness, *ca.* 14-16%. This

corresponded to the volume shrinkage of *ca.* 36-42%. The densities of the sintered ceramics were measured, giving the results of *ca.* 95-98% in relative to the crystallographic density,  $4.62 \text{ gcm}^{-3}$ . No correlation between the obtained values and the variation in synthesis reaction time could be observed, although the powders obtained from the reactions with the prior ultrasonication showed slightly better volume shrinkage and densification. The shrinkage and relative densities of *ca.* 40-42% and 96-98%, respectively, could be calculated for the ultrasonication cases, when the shrinkage of 36-39% with the corresponding relative densities of *ca.* 95% were obtained for the other cases. This could be due to the better defined particle shape and less melting between the particles in the former case as revealed by the SEM images.

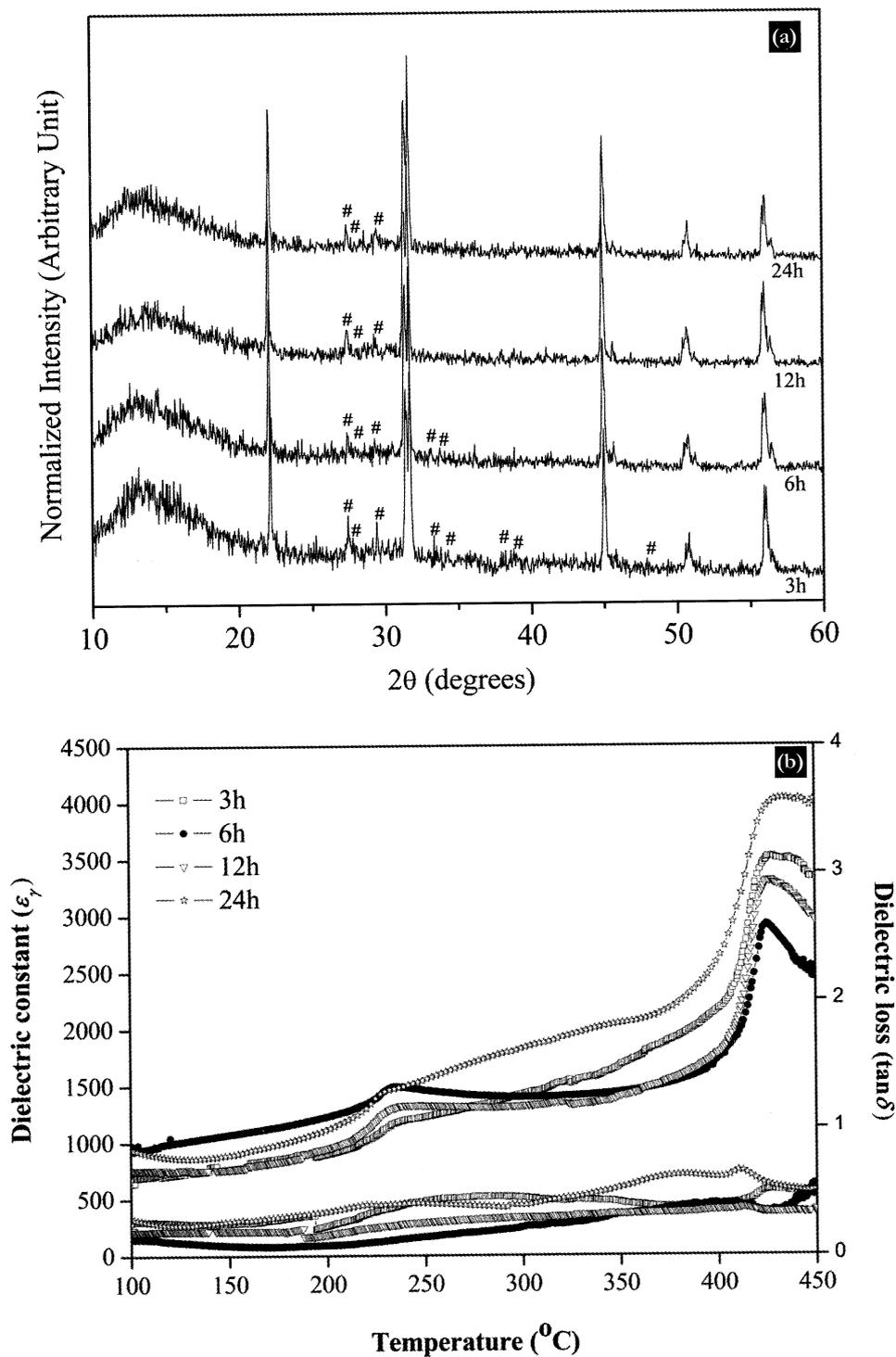
The SEM images taken on the sintered KN pellets gave supportive evidence, as exemplified in Figure 5. The grain sizes of the sintered ceramic were measured and a slight growth of the sintered grain was revealed;  $0.15\text{-}3.95 \mu\text{m}$  and  $0.25\text{-}4.45 \mu\text{m}$  for the short and long axes. These results agree well with the calculated volume shrinkages and the calculated relative densities. It is apparent that the growth process occurred better along the short axis than the long axis, and resulted in an evolution of a pseudo-cubic grain from the pressurized lumber particles. It is also evident that the melting between grains was serious for the pellets which were prepared from the powders derived from prolonged solvothermal reaction, particularly those with the prior ultrasonication treatment. Regarding the hygroscopic problem commonly encountered with the sintering of KN [18], it was not the case in this study if the washing of the remaining alkali was performed carefully. The sensitivity to the atmospheric water may therefore attribute to the remaining of KOH which is hygroscopic.

The XRD was used to follow the change in phase, if any, after the sintering and the results are shown in Figure 6(a) and Figure 7(a). The remaining of the orthorhombic KN was significant, although the formation of the niobium-rich phase,  $\text{KNb}_3\text{O}_8$ , suggesting the loss of  $\text{K}_2\text{O}$  during the sintering were evident. A develop of a big lump at low  $2\theta$  region was additionally plain, implying the corruption of the long range order in the structure although the distinction between the three most intense peaks, including (020), (200) and (111), were clearer after the sintering. The exception was apparent for the sintered pellets which were prepared from the powders obtained from 24 h reaction with the prior ultrasonication, where there was no signature of the  $\text{KNb}_3\text{O}_8$  phase in the XRD pattern. This again reflects the merit of the application of the prior ultrasonication.

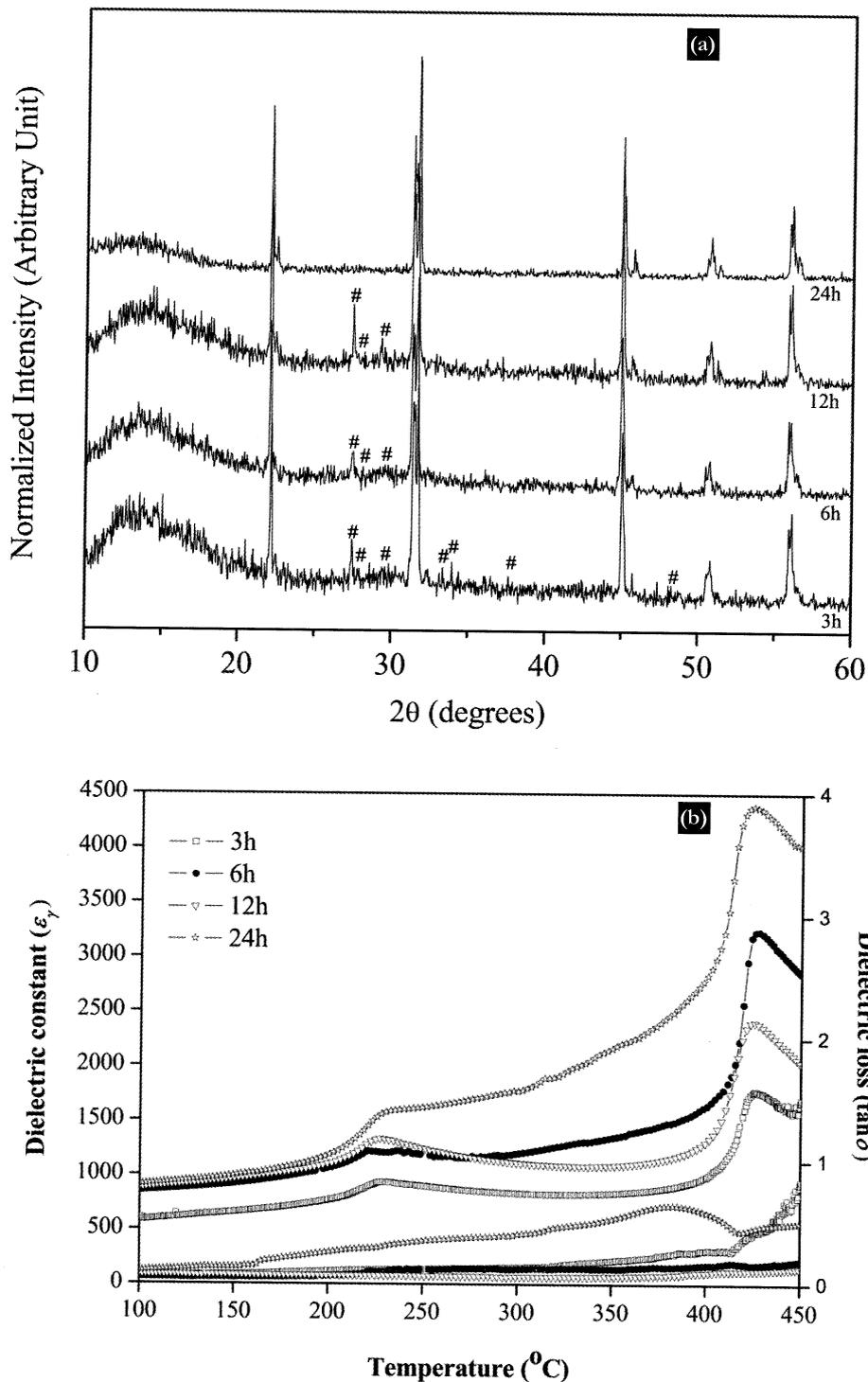
Figure 6(b) and Figure 7(b) show the temperature dependence of dielectric constants ( $\epsilon_p$ ) and dielectric loss tangents ( $\tan \delta$ ) at 100 kHz for the sintered KN ceramics, revealing a difference in the measured values depending on the purity of KN according to the XRD patterns shown in the corresponding Figure 6(a) and Figure 7(a), respectively. Phase transition from the ideal cubic phase to the tetragonal phase was found around  $425^\circ\text{C}$ , while the tetragonal to the orthorhombic occurred around  $225^\circ\text{C}$ . The results are well consistent with the formerly reported values for the KN ceramics [18-21]. In the case of the ceramic composing of KN as nearly a single phase which was the one derived from the powders prepared from 3 h - 24 h reaction with the prior ultrasonication, the dielectric constants has increased with also a sharp peak transition, especially for the KN ceramics of high densities and good crystallinity. The KN ceramics which were fabricated from the powders prepared from the same conditions but without the prior ultrasonication, showed



**Figure 5.** The SEM images of the sintered KN ceramics prepared from the powders obtained from the reactions conducted at 200°C for (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h on the mixtures without the prior ultrasonication, compared with those of the sonicated mixtures; (e) 3 h, (f) 6 h, (g) 12 h and (h) 24 h.



**Figure 6.** (a) The XRD patterns (# = KNb<sub>3</sub>O<sub>8</sub>) and (b) temperature dependence of dielectric properties measured on the KN ceramics prepared from the powders obtained from the reactions conducted at 200°C for (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h on the mixtures without the prior ultrasonication.



**Figure 7.** (a) The XRD patterns ( $\# = \text{KNb}_3\text{O}_8$ ) and (b) temperature dependence of dielectric properties of the KN ceramics prepared from the powders obtained from the reactions conducted at 200°C for (a) 3 h, (b) 6 h, (c) 12 h and (d) 24 h on the mixtures with the prior ultrasonication.

a broad peak transition, which should probably be due to the presence of the liquid phase in microstructure. This results were consistent with the XRD and SEM results that showed the formation of the second phase  $\text{KNb}_3\text{O}_8$  and the liquid phase in the microstructure due to the evaporation of  $\text{K}_2\text{O}$ . In general, it was evident that the ceramics prepared from the powders which were derived from the reactions with the prior ultrasonication showed higher dielectric constants and lower dielectric loss than those without the prior ultrasonication. This may attribute to the increase in oxygen vacancies which on the other hand contribute to the increase in conductivity [22].

#### 4. CONCLUSIONS

In summary, the sonocatalyzed ethano-thermal process has been attempted with the synthesis of potassium niobate fine powders, and proved to be able to provide the orthorhombic phase-pure KN powders under mild condition and rapid reaction times of at least 3 h. The use of mixed water-ethyl alcohol liquid medium apparently favored the formation of elongated lumber KN particles of sub-micrometer sizes, when the application of the prior ultrasonication on the reaction mixtures led to significant differences in sintering behavior, loss of  $\text{K}_2\text{O}$  and the tolerance of the orthorhombic KN to the sintering, as well as the corresponding dielectric properties. Dense KN ceramics of over 95% relative densities could be fabricated by conventional sintering without the hygroscopic problem. The significance of the prior ultrasonication on the reaction mixtures during the synthesis in enhancing both physical and electrical properties of the sintered ceramics was clearly illustrated.

#### ACKNOWLEDGEMENTS

The Thailand Research Fund is

acknowledged for financial support. K. Jinachai thanks to Department of Chemistry, Faculty of Science and the Graduate School, Chiang Mai University for a teaching assistant scholarship.

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