

Phase and morphology evolution of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders related to calcinations and K_2CO_3 content

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Abstract

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Sodium-potassium niobate $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders with $x = 0.2, 0.4, 0.6$ and 0.8 were prepared following the conventional mixed oxide method and characterized by TG-DTA, XRD and SEM techniques. The effects of calcination temperature, dwell time and K_2CO_3 content on phase formation behavior and morphology of the powders were investigated. The calcination temperature and dwell time were found to have a pronounced effect on the phase formation of the calcined sodium-potassium niobate powders. It was found that the crystallized phase depended on calcination conditions. The high calcination temperature and long dwell time clearly favored particle growth and the formation of large and hard agglomerates. All the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders showed a similar orthorhombic phase structure. The K_2CO_3 content significantly affected the calcination temperature and particle size and shape. Large particle size, cubic shape and a lower calcined condition were observed in $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powder with low K_2CO_3 content ($x = 0.2$).

Key words : sodium-potassium niobate, lead-free piezoelectric material, phase formation, morphology evolution

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บทคัดย่อ

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 การเกิดเฟสและสัณฐานวิทยาของผง $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ ที่สัมพันธ์กับการแคลไซน์และ
 ปริมาณโพแตสเซียมคาร์บอเนต

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ผงโซเดียม-โพแตสเซียมไนโอเบต $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ เมื่อ x มีค่า 0.2 0.4 0.6 และ 0.8 เตรียมขึ้นโดยใช้วิธีการผสมออกไซด์แบบที่ใช้กันทั่วไป และนำไปตรวจสอบด้วยเทคนิคที่จี-ดีทีเอ (TG-DTA) การเลี้ยวเบนของรังสีเอ็กซ์ (XRD) และกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราด (SEM) โดยทำการศึกษาอิทธิพลของอุณหภูมิที่ใช้ในการเผาแคลไซน์ เวลา และปริมาณของโพแตสเซียมคาร์บอเนตที่ส่งผลต่อพฤติกรรมการก่อเกิดเฟสและลักษณะทางสัณฐานวิทยาของผงที่เตรียมได้ จากผลการทดลองพบว่าอุณหภูมิและเวลาที่ใช้ในการเผาแคลไซน์มีผลต่อการเกิดเฟสของผงโซเดียม-โพแตสเซียมไนโอเบต คือ การเกิดเฟสที่เป็นผลึกขึ้นอยู่กับเงื่อนไขที่ใช้ในการแคลไซน์ ซึ่งอุณหภูมิแคลไซน์ที่สูงและใช้เวลาในการเผานานส่งผลต่อการโตของอนุภาคและการเกิดกลุ่มของอนุภาคที่แข็งและมีขนาดใหญ่ ผงโซเดียม-โพแตสเซียมไนโอเบตมีโครงสร้างผลึกแบบออร์โธโรมบิกเหมือนกันทุกอัตราส่วน ปริมาณของโพแตสเซียมคาร์บอเนตมีผลอย่างมีนัยสำคัญต่ออุณหภูมิแคลไซน์ รวมทั้งขนาดและรูปร่างของอนุภาค โดยที่อนุภาคขนาดใหญ่ รูปร่างเป็นรูปทรงสี่เหลี่ยมและการเผาแคลไซน์ได้ที่อุณหภูมิต่ำพบในผงโซเดียม-โพแตสเซียมไนโอเบตที่มีปริมาณโพแตสเซียมคาร์บอเนตต่ำ ($x = 0.2$)

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Lead oxide-based ferroelectrics, represented by lead zirconate titanate $(\text{Pb}(\text{Zr,Ti})\text{O}_3$ or PZT) for example, are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties (Guo *et al.*, 2004; Jaffe *et al.*, 1971). Because of the detrimental effects of lead (Pb) on human health, the environmental problems caused by the emission of PbO vapors, the problems of safe disposal of waste chemicals and the difficulties in removing Pb during component recycling, it is imperative that new ferroelectric, pyroelectric and piezoelectric materials be developed. The new environmentally acceptable and biocompatible materials must exhibit electrical properties at least comparable to those of Pb- based ferroelectrics which have been developed over the past four decades.

Sodium-potassium niobate $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ ceramics are considered to be one of the candidates for an alternative system (Guo *et al.*, 2004; Guo *et al.*, 2005). This material is a combination of ferroelectric KNbO_3 and antiferroelectric NaNbO_3

(Guo *et al.*, 2004; Shirane *et al.*, 1954; Wang *et al.*, 2004). Generally, the mixed oxide method involves heating of the mixture of this material above 800°C (Guo *et al.*, 2004; Guo *et al.*, 2005; Singh *et al.*, 2001; Wang *et al.*, 2004). However, the relationship between the phase formation and calcination condition of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ system over a large composition range has not yet been clarified, and the optimization of calcination conditions used in the mixed oxide process for this material have not received detailed attention. The aim of this work was, therefore, to investigate the phase formation and morphology of the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders calcined at various conditions.

Materials and methods

Samples were prepared by the conventional mixed oxide process with reagent grade starting materials of NaCO_3 , K_2CO_3 and Nb_2O_5 (Aldrich Chemical Company, Inc., 99.9+% purity). The use

of two different powders with carbonate origin requires extra care to be taken against humidity. Thermogravimetric analysis (TGA) showed that the powders lose weight up to 120°C , which is equivalent to the water absorbed. Therefore, in order to obtain the stoichiometric material composition, all powders were separately dried in an oven at 150°C for 24 h prior to mixing. The starting materials with the nominal composition of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ (with $x = 0.2, 0.4, 0.6$ and 0.8) were weighed and transferred to a plastic jar, which was previously filled with 10 mm-diameter alumina grinding balls. They were ball milled for 24 h using ethanol as the medium. Drying was carried out at around 120°C for 24 h. The powders were then ground to break a soft agglomeration from drying. A $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$, which is a middle composition, was firstly calcined at various calcination conditions, i.e. temperatures ranging from 600 to 950°C , dwell times ranging from 2 to 10 h. The other compositions of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders ($x = 0.2, 0.6$ and 0.8) were then calcined at the optimized conditions from $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powder.

The reactions of the TG-DTA curves for the uncalcined mixture of $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Nb}_2\text{O}_5$ with

a mole ratio $0.6 : 0.4 : 1$, respectively, taking place during heat treatment were observed by thermogravimetric and differential thermal analysis (TG-DTA, Perkin Elmer TGA7), using a heating rate of $10^\circ\text{C}/\text{min}$ from room temperature up to 1200°C . Calcined powders were subsequently examined by room temperature X-ray powder diffraction (XRPD; Philips X' Pert MPD), using Ni-filtered CuK_α radiation to identify the phase formed and optimum calcination conditions for preparation of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powder. Miller indices of diffraction peaks marked in the figures are indexed on the basis of the standard JCPDS data for orthorhombic NaNbO_3 [(PDF # 33-1270)]. Powder morphologies and particle sizes were directly imaged, using scanning electron microscopy (SEM; Jeol : JSM-5800LV).

Results and discussion

The TG-DTA analysis of a powder mixed in the stoichiometric proportions of $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ is given in Figure 1. The TG curve showing overall weight loss was equal to 11.5% from room temperature to 1200°C . It showed a 0.4% weight loss

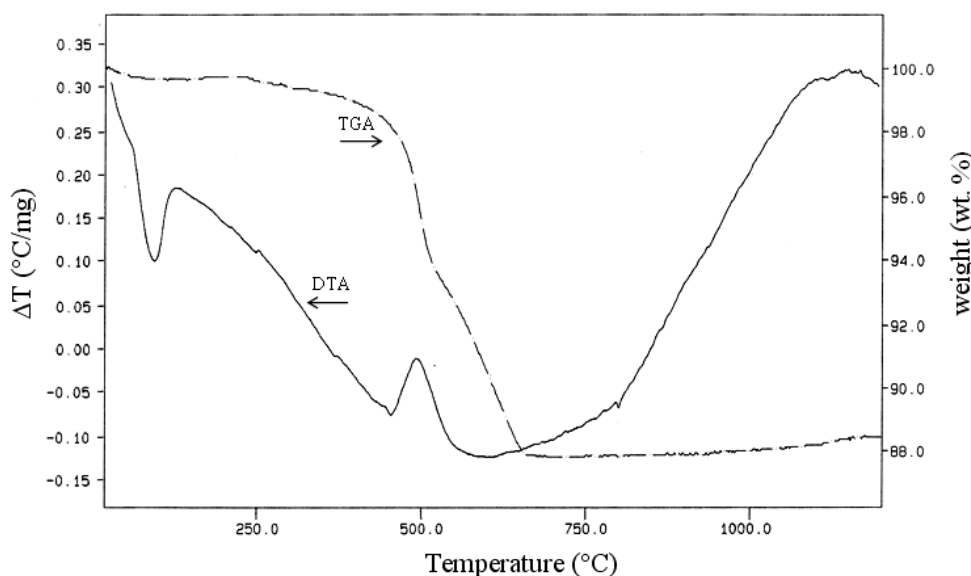


Figure 1. TG-DTA curves for the mixture of $\text{Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-Nb}_2\text{O}_5$ with a mole ratio $0.6 : 0.4 : 1$, respectively.

between 25 and 200°C. In the same temperature range, the DTA curve showed an endothermic peak positioned at around 93.02°C, which is associated to the decomposition of water molecules. The decrease in weight of around 10%, occurring in the temperature range between 440 and 650°C, was correlated with the exothermic peak of DTA curve at 495.59°C. The crystallization of sodium-potassium niobate was, therefore, observed at around 495.59°C. No further significant weight loss was observed for temperatures above 650°C, indicating an absence of decomposition and/or volatilization of Na and K oxides after forming to sodium-potassium niobate. These TG-DTA data were used to define the range of temperatures for calcination.

To further investigate the phase formation with increasing calcination temperature in the $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powders, they were calcined for 2 h in air at various temperatures, up to 950°C. The powder calcined at a temperature below 800°C for 2 h, it was found that unreacted precursors of Nb_2O_5 and K_2CO_3 were detected due to the formation of reaction was still incomplete during the low firing process. X-ray diffraction patterns of $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powders are shown in Figure 2. After calcination at 800°C, the major Bragg peaks corresponding to the expected sodium-potassium niobate phase were obtained (Guo *et al.*, 2005; Birol *et al.*, 2005). All peaks of the powders coincided well with those of NaNbO_3 (PDF # 33-1270), suggesting that calcination temperatures ranging from 800-950°C for 2 h converted the mixed oxides of Na_2CO_3 , K_2CO_3 and Nb_2O_5 to a single phase, which was observed to be a perovskite structure (Zhang *et al.*, 2006). However, a slight displacement of the 2θ position to lower values was observed with relation to the positions of NaNbO_3 (PDF # 33-1270). With calcination at 800°C the expected orthorhombic phase for this powder could not be indexed as the peak splitting characteristic of that phase at the 2θ angles of the diffraction peaks around 45-47° and 51-52° did not appear. The crystalline and single phase was, then, obtained after being calcined at 850°C. This result revealed that the increase of calcination temper-

ature leads to an increase of the crystallinity accompanied by an increase of diffraction peak intensities and a simultaneous decrease in the breadths of the peaks.

Apart from the calcination temperature, the effect of dwell time was also investigated. Three dwell times (2, 6 and 10 h) were selected for calcination condition at 900°C as a full crystallization of sodium-potassium niobate phase was obtained at this temperature. It was found that there was no significant difference for XRD patterns of powders (Figure 3) with increasing dwell time ranging from 2 to 10 h. It is obvious that a full crystallization of single phase for sodium-potassium niobate was found to be possible in powders calcined at 900°C with a dwell time of 2 h or more (yield of 100% within the limitations of the XRD technique).

The effect of K_2CO_3 content for $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ ($x = 0.2, 0.4, 0.6$ and 0.8) powders was also investigated and found to be quite significant (Figure 4). Similar XRD patterns for all powders calcined at 900°C for 2 h were observed, suggesting the formation of a single phase solution with a perovskite structure over the whole composition range. All diffraction peaks of the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders coincided well with those of NaNbO_3 (PDF # 33-1270) or KNbO_3 (PDF # 71-0946). However, a slight shift of the diffraction peaks, such as around 22-23°, 31-32°, 45-47°, 51-52°, 56-57° and 66-67°, with increasing K content was observed. The d-spacing values of powders were, therefore, found to increase from the NaNbO_3 side to the KNbO_3 side. As reported earlier, Shirane *et al.* showed the phase structure of a NaNbO_3 - KNbO_3 system in detail using XRPD. They found that the corresponding lattice parameters decreased continuously from the KNbO_3 side to NaNbO_3 (Shirane *et al.*, 1954). The completely crystallized phase was found in all compositions, except at $x = 0.6$, because the minor amount of unreacted precursor of K_2CO_3 still appeared. It is suggested that the single phase of sodium-potassium niobate depended on the K_2CO_3 content. All the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders showed a similar orthorhombic phase structure (Zhang *et al.*, 2006; Jaffe *et al.*,

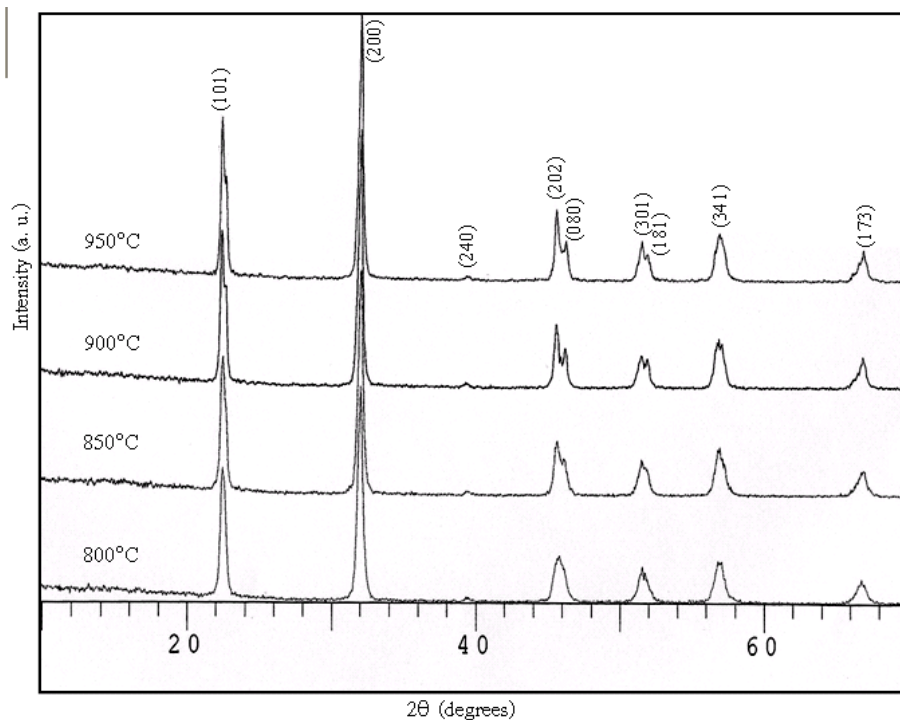


Figure 2. XRD patterns of $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powder calcined at various temperatures for 2 h.

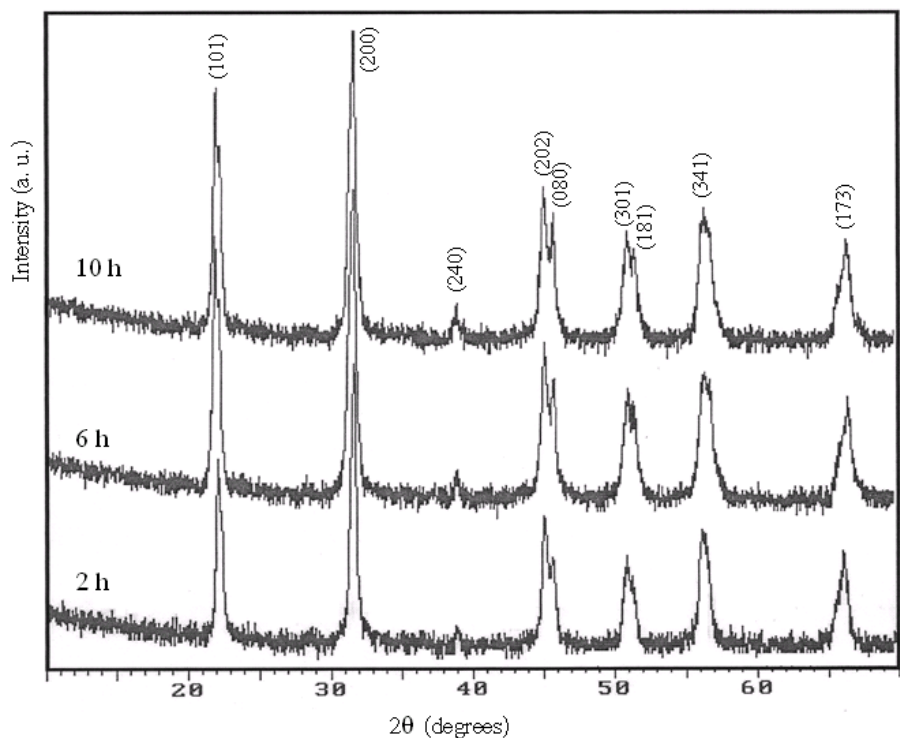


Figure 3. XRD patterns of $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powder calcined at 900°C with various dwell times.

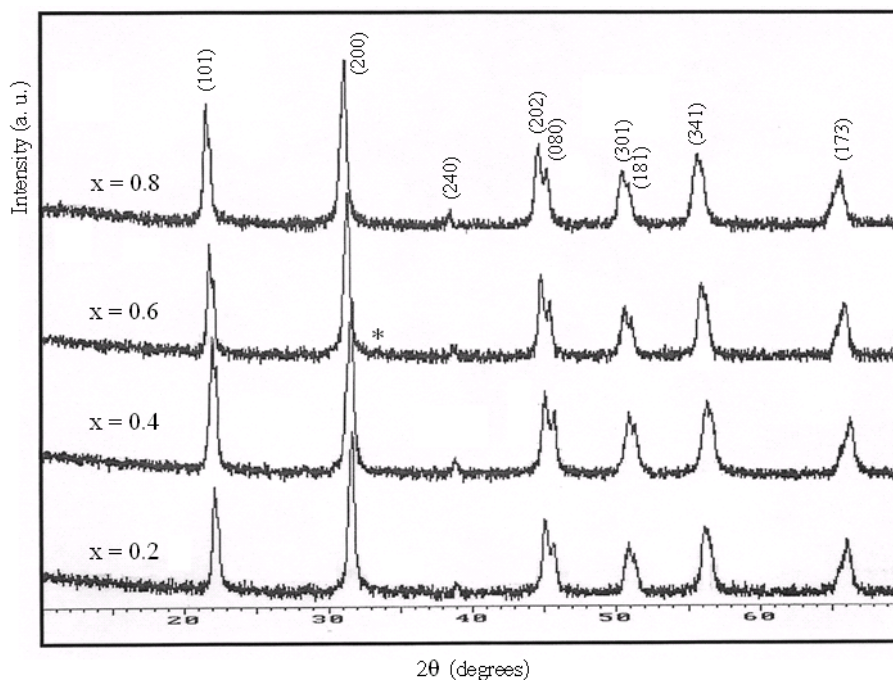


Figure 4. XRD patterns of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powder calcined at 900°C for 2 h (* = K_2CO_3).

1971).

The morphological evolutions in the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders formed by a mixed oxide are illustrated in Figures 5-6 as a function of calcination temperatures, dwell time and K content. The effect of calcination conditions and the K_2CO_3 content on particles size is displayed in Table 1. In general, the particles were agglomerated and basically irregular in shape, with a substantial variation in particle size, particularly in samples calcined at high temperature (Figure 5(b)). The effect of dwell time on the morphology of the calcined powders was also found to be quite significant. It is clearly seen that longer heat treatment led to larger particles and hard agglomeration (Figure 5(c)). This finding was also similar to that in NiNb_2O_6 or ZnNb_2O_6 powders (Khamman *et al.*, 2006; Ngamjarrojana *et al.*, 2006). The results indicated that differences in particle size and degree of agglomeration tend to increase with increasing temperature and dwell time (Table 1). After calcination at 900°C for 2-10 h, the powders seem to display a significant level of bonding as

if they were in the initial stages of sintering (Figure 5(c)), and the shape of the powders tends to cubic. The samples with various K_2CO_3 contents showed differences in particles size and shape (Figures. 5 (b), 6). As can be seen, the larger particle and shape tending to cubic were found in the sample with low K_2CO_3 content ($x = 0.2$). After increasing the K_2CO_3 content up to $x = 0.8$, the particle size decreased and the shape was basically irregular. This result showed that the content of K_2CO_3 significantly affected the calcination temperature because of powders seem to display a significant level of necking and bonding as if they were in the initial stages of sintering. Hence, a low K_2CO_3 content sample could synthesize with a lower temperature than 900°C for 2 h.

Conclusion

The $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ ($x = 0.2-0.8$ mol) powders were prepared by a solid state reaction. Evidence gained from XRD revealed that a complete single crystallized phase of orthorhombic phase structure

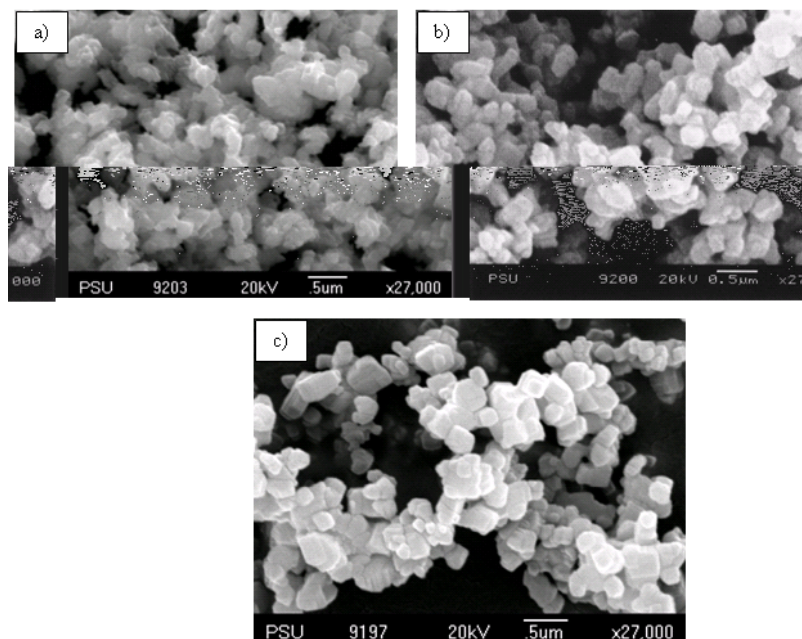


Figure 5. SEM micrographs of the $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powder calcined at various conditions; a) 800°C for 2 h, b) 900°C for 2 h, and c) 900°C for 10 h

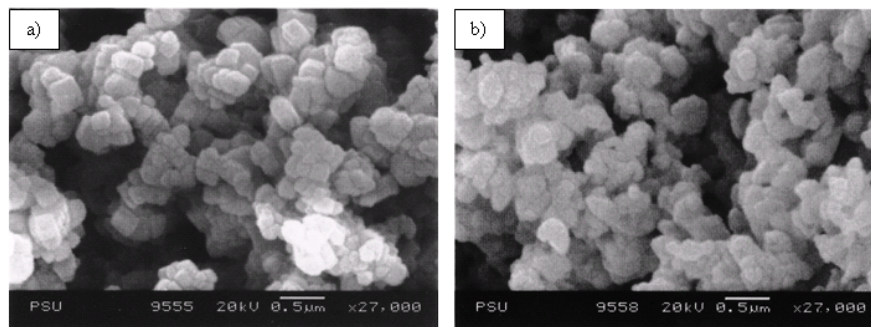


Figure 6. SEM micrographs of the $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders calcined at 900°C for 2 h; a) $x = 0.2$ and b) $x = 0.8$.

Table 1. Particle size range of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders calcined at various conditions.

Calcination conditions		K_2CO_3 content (mol)	Particle size range (± 10 nm)
Temperature ($^{\circ}\text{C}$)	Dwell time (h)		
800	2	0.4	140-180
900	2	0.4	160-270
900	10	0.4	170-420
900	2	0.2	170-310
900	2	0.8	150-200

of $(\text{Na}_{0.6}\text{K}_{0.4})\text{NbO}_3$ powder with particle size ranging from 160-270 nm could be obtained in this study after being calcined at 850°C for 2 h. The formation of a single phase solution of $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ with a orthorhombic structure was produced in the whole composition range when calcined at 900°C for 2 h, except when $x = 0.6$, due to the minor amount of unreacted precursor of K_2CO_3 still remaining. It is suggested that the single phase of sodium-potassium niobate depended on the K_2CO_3 content. The corresponding d-spacing values of powders increased continuously from the NaNbO_3 side to KNbO_3 side. The resulting $(\text{Na}_{1-x}\text{K}_x)\text{NbO}_3$ powders consist of a variety of agglomerate particles sizes and shape, depending on calcination condition and amount of K_2CO_3 .

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