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## Phase and Morphology Evolution of Sodium-Potassium Niobate Powder Synthesized by Solid-State Reaction

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### Abstract

Sodium-potassium niobate ((Na<sub>0.5</sub>K<sub>0.5</sub>)NbO<sub>3</sub>) powders were prepared following the conventional mixed oxide method and characterized by TG-DTA, XRD and SEM techniques. The effect of calcination temperature, dwell time and excess of starting powders on phase formation 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 depends on calcination conditions. An excess of Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub> starting powders clearly favored particle growth and the formation of large and hard agglomerates.

### 1. Introduction

Lead oxide based ferroelectrics, represented by lead zirconate titanate (Pb(Zr,Ti)O<sub>3</sub> or PZT) for example, are widely use for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [1,2]. 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 ((Na<sub>1-x</sub>K<sub>x</sub>)NbO<sub>3</sub> or NKN) ceramics are considered to be one of candidates as the alternative systems [1,3]. (Na<sub>1-x</sub>K<sub>x</sub>)NbO<sub>3</sub> is a combination of ferroelectric KNbO<sub>3</sub> and antiferroelectric NaNbO<sub>3</sub>, and

forms a morphotropic phase boundary (MPB) near 50/50 composition ( $x = 0.5$ ) separating two orthorhombic phases [1,4-5]. Generally, the mixed oxide method involves the heating of mixture of this material above 800 °C for long time [1,3,5]. The optimization of calcination conditions for this material, however, have not received detailed attention, the excess of starting powder have not yet been studied extensively. The aim of this work was, therefore, to investigate the phase formation and morphology of the powder calcined at various conditions.

### 2. Experimental procedure and methods

Samples were prepared by the conventionally mixed oxide process with the reagent grade of starting materials of NaCO<sub>3</sub>, K<sub>2</sub>CO<sub>3</sub> and Nb<sub>2</sub>O<sub>5</sub> (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) shows 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 stoichiometric amounts of starting powders 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 120 °C for 3 h, prior to grinding. After grinding, the mixtures were calcined at various calcination conditions in an alumina crucible, i.e. temperatures ranging from 800 to 950 °C, dwell times ranging from 2 to 10 h and addition of starting powders (Na<sub>2</sub>CO<sub>3</sub> and K<sub>2</sub>CO<sub>3</sub>) up to 5 mol%, in order to investigate the formation of (Na<sub>0.5</sub>K<sub>0.5</sub>)NbO<sub>3</sub>. The reactions of the

uncalcined NKN powders taking place during heat treatment were observed by thermogravimetric and differential thermal analysis (TG-DTA, Perkin Elmer TGA7), using a heating rate of 10 °C/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  $\text{CuK}\alpha$  radiation to identify the phase formed and optimum calcination conditions for preparation of NKN powder. Powder morphologies and particle sizes were directly imaged, using Scanning electron microscopy (SEM; Jeol : JSM-5800LV).

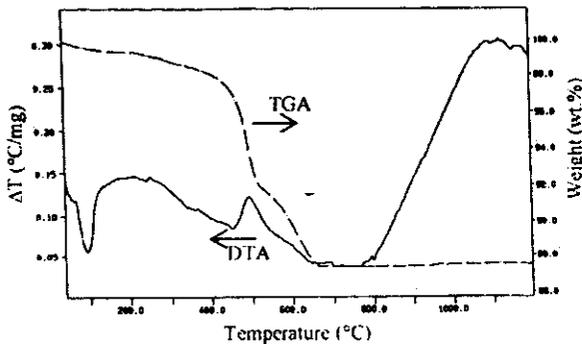


Fig.1 TG-DTA curves for the mixture of  $\text{Na}_2\text{CO}_3$ - $\text{K}_2\text{CO}_3$ - $\text{Nb}_2\text{O}_5$ .

### 3. Results and Discussion

The TG-DTA analysis of a powder mixed in the stoichiometric proportions of  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  is given in Fig.1. The TG curve showing overall weight loss was equal to 12.5% from room temperature to 1200 °C. It shows a 0.5% weight loss between 25 and 200 °C. In the same temperature range, the DTA curve shows an endothermic peak positioned at around 94.39 °C, which is associated to the decomposition of water molecules. According to TGA curve, the highest weight loss attains value at around 10%, occurring between 465 and 650 °C. This loss is correlated with the exothermic peak at 495.14 °C, in accordance with DTA curve. The crystallization of sodium-potassium niobate was, therefore, observed at 495.14 °C. No further significant weight loss was observed for the temperature above 650 °C, indicating an absence of decomposition above this temperature. These TG-DTA data were used to define the range of temperatures for calcination.

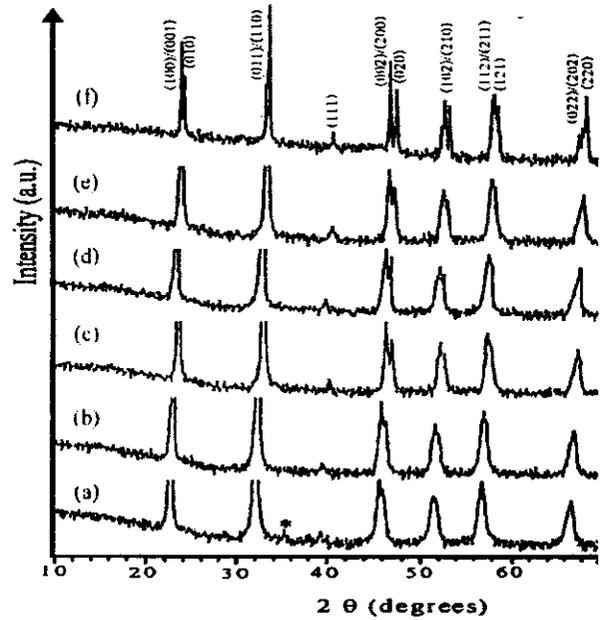


Fig.2 XRD patterns of NKN powder calcined at various conditions; a) 800 °C for 2 h, b) 850 °C for 2 h, c) 900 °C for 2 h, d) 950 °C for 2 h, e) 900 °C for 10 h and f) with an excess of 0.05 mol of starting materials (\* =  $\text{K}_2\text{CO}_3$ ).

To further investigation the phase formation with increasing calcination temperature in the powders, they were calcined for 2 h in air at various temperatures, up to 950 °C. X-ray diffraction patterns of NKN powders are shown in Fig. 2. After calcination at 800 °C, the major Bragg peaks corresponding to the expected orthorhombic sodium-potassium niobate (NKN) phase are obtained [3,6] accompanying with  $\text{K}_2\text{CO}_3$  as a minor phase. The crystalline and single phase is obtained after calcined at 850 °C. The increase of calcination temperature leads to an increase of the crystallinity accompanied by increase of diffraction peak intensities and a simultaneous decreasing in their breadths of peaks. Apart from the calcination temperature, the effect of dwell time and an excess of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  were also investigated. Three dwell times (2, 6 and 10 h) were selected for calcination condition at 900 °C. A full crystallization of NKN phase was obtained at this temperature. It is found that there is no significant difference for XRD patterns of powders with increasing dwell time ranging from 2 to 10 h (see in Fig. 2(e)). It is obvious that a full crystallization of NKN phase was obtained in this study at lower time than the previous work [5] and it provided more

crystallized phase than other investigations [1,3,5-6]. For addition of excess starting materials, three amounts (0, 0.03 and 0.05 mol) were selected for calcination condition at 900 °C for 2 h. It can be seen that the single phase of NKN is still observed with increasing the amount of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  up to 0.05 mol (Fig. 2(f)).

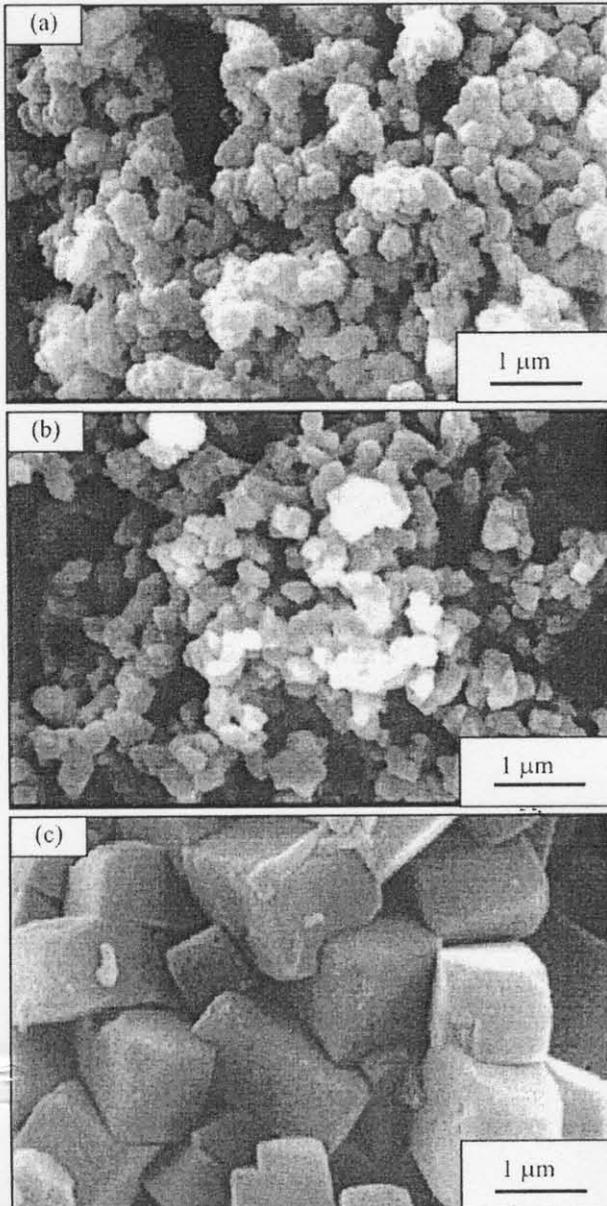


Fig.3 SEM micrographs of the NKN powders calcined at various conditions; a) 900 °C for 2 h, b) 900 °C for 10 h, and c) with an excess of 0.05 mol of starting materials.

The morphological evolutions in the  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  powders are illustrated in Fig. 3 as a function of

calcination temperature, dwell time and the excess of starting powders. In general, the particles are agglomerate and basically irregular in shape (Fig. 3 (a-b)). Particle size tends to increase with increasing temperature and dwell time ranging from 0.14 to 0.30  $\mu\text{m}$  for powder calcined at 900 °C for 2 h and 0.27 to 0.41  $\mu\text{m}$  for powder calcined at 900 °C for 10 h. The sample with 0.05 mol excess of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  shows large cubic particles with particle size ranging from 1 to 2  $\mu\text{m}$  (Fig. 3(c)). This result shows that the addition of an excess  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$  can significantly reduce the calcination temperature to lower temperature than 900 °C for 2 h.

#### 4. Conclusion

The  $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$  powder is prepared by a solid state reaction. Evidence gained from XRD revealed that a completely single crystallized phase with particle size ranging from 0.14 to 0.30  $\mu\text{m}$  was obtained in this study by using a calcination temperature at 900 for 2 h. The resulted NKN powders consist of a variety of agglomerate particle sizes, depending on calcination condition and amount of an excess of  $\text{Na}_2\text{CO}_3$  and  $\text{K}_2\text{CO}_3$ .

#### 5. Acknowledgment

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