# A new way of synthesis of non-linear optical potassium niobate powder

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Potassium niobate ($KNbO_3$) (KN) is a ferroelectric material having high electro-optic and non-linear optical coefficients and excellent photo-refractive characteristics. Furthermore, $KNbO_3$ has large piezoelectric constants. This material attracts great interest for application in optical waveguides, frequency doubles and holographic storage systems [1–4].

In general, the fundamental synthesis processes for ceramics basically use heat treatment for the reaction of mixed raw materials [5, 6]. The reaction rate of these kinds of processes is limited by solid state diffusion. For example, synthesis of $KNbO_3$ requires 30 h of heating [7] of the reactants at 1273 K and cooling at a very slow rate. Fig. 1 shows the phase diagram [8] of $K_2O$-$Nb_2O_5$ components. Single crystals are grown from the $KNbO_3$ + liquid phase. However, the high-temperature heating not only is energy consuming, but also causes unfavourable grain growth of particles of the reaction product, and pure phase $KNbO_3$ is difficult to obtain [9].

When solution processes, such as sol–gel and precipitation methods are used, $KNbO_3$ can be obtained, but the required calcinations temperature has to be higher than 600 °C [10, 11]. In order to reduce the synthesis time of $KNbO_3$, microwave assisted solid-state synthesis of potassium niobate has been reported with considerably shorter reaction times. The method takes less than 20 min for the preparation and good crystalline products of high phase purity are obtained [12]. For reducing the synthesis temperature of $KNbO_3$, hydrothermal synthesis of potassium niobate has been reported by Chung-hsin Lu *et al.* [13, 14]. When KOH, with a concentration of 8 M reacted with $Nb_2O_5$ particles at 200 °C, monophasic $KNbO_3$ was obtained.

We report here the high concentration medium of caustic potash synthesis of micro crystalline, single phase $KNbO_3$ through the reaction of commercial $Nb_2O_5$ with KOH (65–68%) at 200 °C under atmospheric pressure. The conditions for obtaining $KNbO_3$ in the reaction were first determined. Then the effect of the amounts of raw materials on the morphology of the reaction product was analyzed.

All the chemical reagents employed were of analytical grade and the deionized water was used for the experiments. The niobium pentoxide used was supplied by the Ningxia Orient Tantalum Industry Co., Ltd, which is located in Ningxia municipality, P.R. China.

The batch reactor used in this work was a 400-ml teflon-lined nickel stainless steel canister equipped with a thermometer, a mechanical stirrer and a reflux condenser. The reactor was heated by an oil bath, whose temperature was thermostatically controlled by an electrical bar, with a precision of $\pm 1$ °C. Fig. 2 illustrates the experimental apparatus used in this work.

All the experiments were conducted in batches. For each run, 130 g solid KOH was first charged into the reactor, and deionized water of the required amount was added. Then the system was heated to the required temperature under continuous stirring. When the temperature reached the pre-set value and remained stable, a certain amount of niobium pentoxide was added to the reactor. Then, the mixture of all the reactants was intensively stirred under atmospheric pressure. After maintaining for the required time, the reactor was taken out from oil-bath, cooled immediately by force air, the obtained powders were washed with pure water and finally dried in an oven to remove the absorbed water at 105 °C for 12 h. The compounds present in the powders were identified via X-ray powder diffraction (XRD, Rigaku D/Max-3c, Cu $K_\alpha$ radiation). The particle size and morphology of the samples were investigated by scanning electron microscopy (SEM, Hitachi Model S-3500N).

Potassium hydroxide was reacted with niobium pentoxide under various conditions and the compounds formed in the obtained products are summarized in Table I. The products determined by X-ray diffraction analysis are classified into four categories (A to D).

It was found that, at 150 °C and a concentration of KOH (50–75%), only a small amount of $Nb_2O_5$ existed in the products, most of $Nb_2O_5$ was converted into soluble potassium niobate, even with the reaction time prolonged to 180 min. When the reaction temperature was 200 °C, and the concentration of KOH was 65–68%, a large amount of $KNbO_3$ was crystallized. With the increase of the concentration of KOH, the amount of $KNbO_3$ decreased steadily. When the concentration of KOH was increased to 85%, after the dissolution of $Nb_2O_5$ in the medium of caustic potash at 200–260 °C, all of $Nb_2O_5$ was dissolved in the solution. However, no precipitates were formed. For a concentration of KOH equal to 75%, a small amount of $KNbO_3$ was obtained after the 200 °C-reaction, however, a large amount of $KNbO_3$ was formed after 260 °C-reaction. The above results reveal that the concentration of KOH

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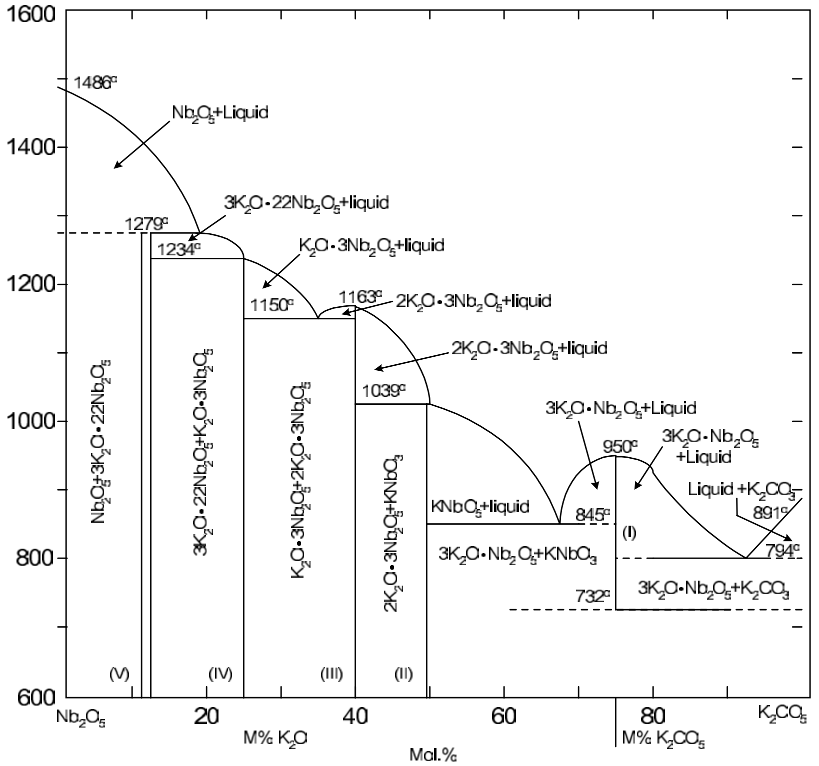
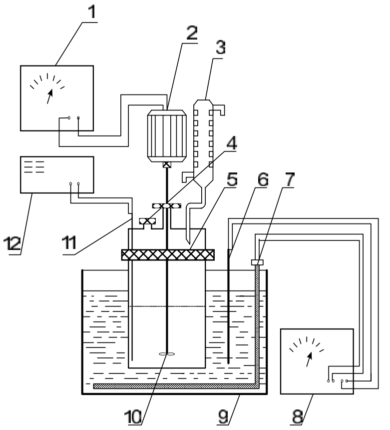


*Figure 1* Phase diagram of $K_2O$-$Nb_2O_5$.



1. AC adjustable voltage speed controller
2. Agitator
3. Reflux condenser
4. Thief hatch
5. Nipple
6. Thermocouple
7. Electrical bar
8. Temperature controller
9. Oil-bath
10. Stirrer
11. Thermocouple
12. Digital display device

*Figure 2* Experimental apparatus.

and temperature are two critical controlling factors for synthesizing $KNbO_3$. At a low temperature, there is no potassium niobate formed, and most of the $Nb_2O_5$ was converted into soluble niobate.

In a parallel experiment, $KNbO_3$ was prepared via the conventional solid-state reaction using $Nb_2O_5$ and KOH particles as raw materials. The mixed raw materials were calcined at elevated temperatures for 2 h. A small amount of $KNbO_3$ appeared after calcination at 500 °C and the formation of $KNbO_3$ became nearly complete at 650 °C. Although the same raw materials were used in both the solid-state and the new process, the reactivity of materials in solid form was apparently inferior to that in solution state. Compared with the solid-state reaction, the new process significantly reduces the synthesis temperature for obtaining pure $KNbO_3$ powders.

As listed in Table I, when the concentration of KOH was fixed at 65% and the reaction temperature was fixed 200 °C, the amounts of $Nb_2O_5$ were accordingly adjusted to be 1, 3 and 6 g, respectively. Under these conditions, the prepared $KNbO_3$ powders were denoted as KN-1, KN-2 and KN-3. The XRD patterns of these three samples are illustrated in Fig. 3.

As shown in Fig. 2, no $Nb_2O_5$ remained in the products. All diffraction peaks were attributed to $KNbO_3$. KN-1, KN-2 and KN-3 exhibited a pseudocubic structure. The XRD patterns of these powders were consistent with that reported in JCPDS No. 32-0822. The above results imply that the addition of various

TABLE I Products formed in the reaction between KOH and $Nb_2O_5$ at various conditions under atmospheric pressure

| No. | Temperature (°C) | Concentration of KOH (%) | Reaction time (min) | Mass of $Nb_2O_5$ (g) | Products |
|---|---|---|---|---|---|
| 1 | 150 | 50 | 30 | 1 | A |
| 2 | 150 | 50 | 180 | 1 | A |
| 3 | 150 | 65 | 30 | 3 | A |
| 4 | 150 | 75 | 30 | 6 | A |
| 5 | 200 | 65 | 30 | 1 | C |
| 6 | 200 | 65 | 30 | 2 | C |
| 7 | 200 | 65 | 30 | 6 | C |
| 8 | 200 | 68 | 30 | 1 | C |
| 9 | 200 | 68 | 30 | 3 | C |
| 10 | 200 | 75 | 30 | 1 | B |
| 11 | 200 | 75 | 30 | 3 | B |
| 12 | 200 | 85 | 30 | 1 | D |
| 13 | 200 | 85 | 30 | 3 | D |
| 14 | 200 | 85 | 120 | 1 | D |
| 15 | 225 | 68 | 30 | 1 | C |
| 16 | 225 | 75 | 120 | 3 | B |
| 17 | 225 | 85 | 180 | 6 | D |
| 18 | 260 | 75 | 30 | 1 | C |
| 19 | 260 | 85 | 180 | 6 | D |

A: a small amount of $Nb_2O_5$; B: a small amount of $KNbO_3$; C: $KNbO_3$; D: No precipitation.

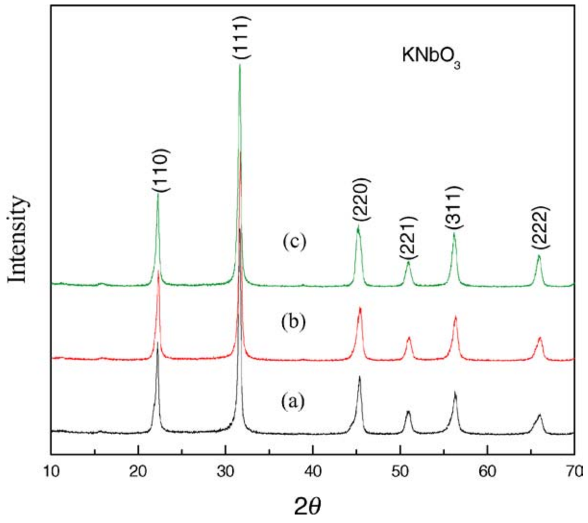


*Figure 3* X-ray diffraction patterns of KNbO$_3$ powders obtained in high concentration medium of caustic potash: (a) KN-1, (b) KN-2 and (c) KN-3.

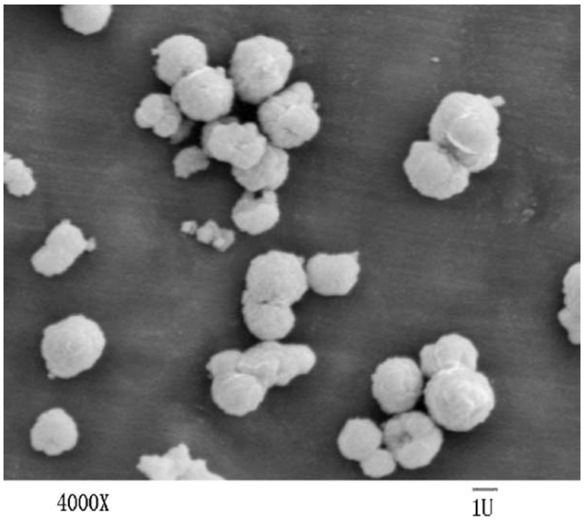


*Figure 4* Scanning electron micrograph of as-prepared KNbO$_3$ powders.

amounts of Nb$_2$O$_5$ has no influence on the crystalline structure of KNbO$_3$.

The microstructure of as-prepared KNbO$_3$ powders is shown in Fig. 3.

Fig. 3 indicates that the ultrafine particles of KNbO$_3$ were obtained in the highly concentrated medium of caustic potash and its morphology was independent of the amount of Nb$_2$O$_5$ used. The particle of the sample exhibited an equal-axial morphology. When the sample was further heated at 1000 °C, its microstructure is shown as Fig. 4; the particle have not changed significantly and particle size was around 2–3 $\mu$m.

In Summary, monophasic KNbO$_3$ powders were successfully prepared in the highly concentrated medium of caustic potash under atmospheric pressure. The synthesis temperature was as low as 200 °C, and the concentration of KOH was 65–68%.

For the traditional solid-state reaction, the temperature for the production of KNbO$_3$ is as high as 650 °C. Using the new process effectively reduced the synthesis temperature of KNbO$_3$. Also, compared to the hydrothermal process, the new process does not need high-pressure equipments, and has more important economical benefit.

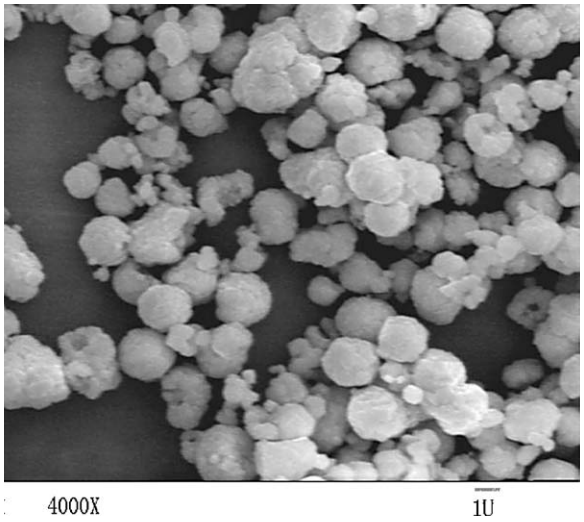


*Figure 5* Scanning electron micrograph of the 1000 °C -heated KNbO$_3$ powders.

The morphology and the particle size of KNbO$_3$ powders were independent of the added amount of Nb$_2$O$_5$ and subsequent heat treatment temperature of KNbO$_3$.

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