

## Hydrothermal Synthesis of $\text{KNbO}_3$ powders in Supercritical water

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The potassium niobate ( $\text{KNbO}_3$ ) powders are synthesized by hydrothermal method in supercritical water. Under such supercritical water conditions, the potassium hydroxide (KOH) concentration employed in the synthesis reaction can be greatly reduced (0.1-0.5M), which is far less than the very high concentration prerequisite to the hydrothermal synthesis of  $\text{KNbO}_3$  powders in subcritical water. The  $\text{KNbO}_3$  powders prepared in supercritical water have rhombohedral and orthorhombic structures depending on the alkaline concentration. It is found that the  $\text{KNbO}_3$  powders with orthorhombic structure exhibit strong second harmonic generation (SHG) intensity.

### 1. Introduction

$\text{KNbO}_3$  with an orthorhombic structure is a well known ferroelectric material, which has promising applications in electromechanical, nonlinear optical and other technological fields [1-5]. Commonly the  $\text{KNbO}_3$  powders are synthesized by solid-state method in which the mixture of reactants is heated under high temperature [6]. In recent years, hydrothermal synthesis method has been successfully applied to prepare  $\text{KNbO}_3$  powders [7-11]. The starting materials for hydrothermal synthesis of  $\text{KNbO}_3$  are niobium pentoxide and the aqueous solution of potassium hydroxide with rather high concentration [8-11]. Usually, only when the alkaline concentration is above 6 M ( $M=\text{mol}/\text{dm}^3$ ),  $\text{KNbO}_3$  can be obtained. In some cases, the KOH concentration is as high as 10 M [8]. Such high alkalinity conditions usually cause the serious corrosion of reaction vessel and inconvenience in waste treatment. The temperature also plays an important role in the hydrothermal synthesis of  $\text{KNbO}_3$ . In previous literatures, hydrothermal temperatures were in the range of 120 to 250°C [8-11], i.e. subcritical water condition. Although Lu et al. have reported the successful glycothermal preparation of  $\text{KNbO}_3$  ceramic particles using 0.5 M KOH in supercritical isopropanol [12], the isopropanol used as supercritical fluid is inflammable, toxic, and may cause serious circumstance pollution. Thus, as an environmentally benign reaction medium, the supercritical water attracts much attention and is introduced into the hydrothermal preparation

process. Recently supercritical water has been proved a preferable reaction medium for oxidation reactions and materials preparations [13,14]. Accordingly, the synthesis of certain materials, such as  $\text{KNbO}_3$  powders, in supercritical water should have significant advantages over those in subcritical water conditions or in supercritical organic fluid.

Here we report that the hydrothermal syntheses of  $\text{KNbO}_3$  powders with either rhombohedral or orthorhombic structures are accomplished in supercritical water with extremely low alkaline concentration. The characterizations for their structure, morphology, and nonlinear optical properties are investigated.

### 2. Experimental Methods

**2.1. Experimental Apparatus** All reagents in this work were used without any pretreatment. Potassium hydroxide (85%, Wako Pure Chemical Industries, Ltd) aqueous solution was mixed with  $\text{Nb}_2\text{O}_5$  fine powder (99.95%, Koso Chemical Co., Ltd), then the mixture was put into a gold tube in the autoclave. The alkaline concentration was 0.1, 0.25 and 0.5 M, and the reaction time was set to be 2, 8 and 24 h. The hydrothermal synthesis was carried out at 400 °C with autogenous pressure of 24 MPa. Upon completion of the reaction, the precipitates were filtrated and washed with distilled water, then dried at 60 °C. In order to make comparison, the  $\text{KNbO}_3$  powder was also prepared using solid-state method [6].

**2.2. Characterization** Crystal structures of resulting powders were determined by the X-ray powder

diffraction (XRD), performed on a Rigaku RINT 2200 diffractometer using  $\text{CuK}\alpha$  radiation (40 kV and 20 mA). The morphology of the prepared  $\text{KNbO}_3$  was observed using a Hitachi S-800 scanning electron microscope (SEM). The second harmonic generation (SHG) response was measured in the reflection mode similar to the method used by Kurtz and Lu et al. [8,15]. The light source is Nd:YAG laser operating at 1064 nm with a repetition rate 10 Hz and a pulse width of 5-7 ns. Urea was used as reference material. The SHG intensity was recorded in reflection with a photomultiplier of MCPD-3000 system (Otsuka electronics Co., Ltd).

### 3. Results and Discussion

**3.1. Structure Characterization** The XRD patterns of the obtained  $\text{KNbO}_3$  powders are shown in Fig.1. Here the reaction time is kept constant as 24 h. When the KOH concentration is 0.1 M,  $\text{KNbO}_3$  polycrystalline powders form and precipitate from solution. The structure of obtained  $\text{KNbO}_3$  powders could be characterized as rhombohedral phase (JCPDS 71-0947). However, a small amount of undissolved  $\text{Nb}_2\text{O}_5$  and the intermediate potassium niobium oxide are found in the final product together with  $\text{KNbO}_3$  powder. When 0.25 M KOH solution is used, rhombohedral  $\text{KNbO}_3$  is obtained without  $\text{Nb}_2\text{O}_5$  except for a weak diffraction peak at 27.6 degree in XRD corresponding to potassium hexaniobate  $\text{K}_4\text{Nb}_6\text{O}_{17}$  (JCPDS 21-1297) as shown in Fig.1b. When the KOH concentration used in the preparation reaches 0.5 M, the obtained  $\text{KNbO}_3$  powders show a different structure which is ascribed to be orthorhombic phase (JCPDS 32-0822).

The influence of reaction time on the components of final product is studied under the KOH concentrations of 0.1, 0.25, and 0.5 M. The crystallization of  $\text{KNbO}_3$  begins when the concentration of KOH is 0.1 M at a reaction time of 8 h. With increasing reaction time, sharp and strong diffraction peaks which are consistent with XRD pattern of rhombohedral  $\text{KNbO}_3$  appear. When the KOH is 0.1 M, the main impurities in the obtained powders are niobium oxide (JCPDS 30-0873) and potassium hexaniobate (JCPDS 21-1297) (marked by circles and asterisks in Fig. 1a). When the KOH concentration is 0.25 M, only a trace of potassium hexaniobate is detected in  $\text{KNbO}_3$  powders for the reaction time of 8 and 24 h. In relatively high alkaline solution such as 0.5 M KOH, the obtained  $\text{KNbO}_3$  powders have pure orthorhombic structure

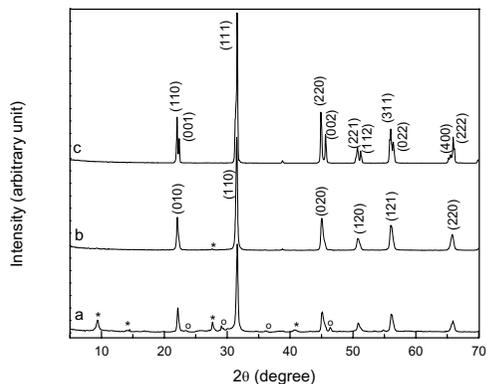


Fig. 1. The XRD patterns of  $\text{KNbO}_3$  powders hydrothermally synthesized in supercritical water with reaction time 24 h; Circles show the existence of  $\text{Nb}_2\text{O}_5$  and asterisks indicate the impurity phase of  $\text{K}_4\text{Nb}_6\text{O}_{17}$ . The KOH concentration is (a) 0.1M, (b) 0.25M, and (c) 0.5M.

and yield good polycrystalline powders with various reaction times of 2, 8 and 24 h. It is confirmed that under constant alkaline condition the structure of  $\text{KNbO}_3$  powders is independent of the reaction time.

**3.2. Morphology Characterization** Figure 2 displays the SEM image of  $\text{KNbO}_3$  powders hydrothermally synthesized in supercritical water. When the KOH concentration is 0.25 M with a reaction time of 24 h, the particles of prepared  $\text{KNbO}_3$  are roughly pyramid-shaped polyhedrons as shown in Fig. 2a. The overall size of the pyramid particle is about 10  $\mu\text{m}$ . Moreover, some of these polyhedron particles have coarse surface. The pyramid-shaped

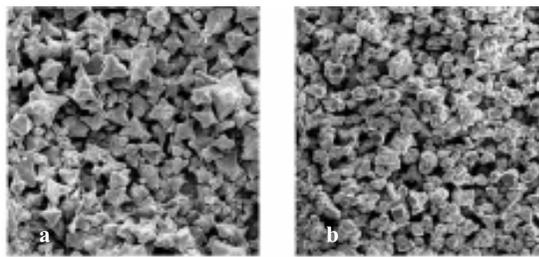


Fig. 2. The SEM images of  $\text{KNbO}_3$  powders hydrothermally synthesized in supercritical water. The experimental condition is: (a) 0.25 M KOH concentration with reaction time 24 h and (b) 0.5 M KOH concentration with reaction time 24 h.

polyhedron particles have rhombohedral  $\text{KNbO}_3$  structure according to XRD characterization. These particles prepared in supercritical water have a larger size and different shape in comparison with  $\text{KNbO}_3$  particles that have with the same structure as that prepared in subcritical water [8,10].

SEM image of  $\text{KNbO}_3$  powders with orthorhombic structure is shown in Fig. 2b. With a short reaction time such as 2 h, most of the particles show irregular polyhedron shape. When the reaction time is increased to be 24 h, the particle shape appears as parallelepiped with the size in the range of 4 to 5  $\mu\text{m}$ . The extended reaction time improves the process of recrystallization and growth of crystal grain, resulting in particles with regular shape.

The properties of supercritical water greatly affect the dissolution of reactants [16,17]. In this experiment, the KOH concentration under normal temperature and pressure is 0.1, 0.25, and 0.5 M. When the experiment is carried out in a supercritical condition system, KOH would precipitate because of its poor solubility in supercritical water, and exist as a molten liquid. In other words, a non-homogenous phase forms [16]. In such a reaction system, the concentration of KOH within the local area is high enough to react with  $\text{Nb}_2\text{O}_5$ . That is why in supercritical water the essential KOH concentration for the reaction is considerably reduced. On the other hand, the low dielectric constant of supercritical water also contributes to the enhancement of reaction kinetics. Therefore, using supercritical water as a reaction medium in the hydrothermal synthesis of  $\text{KNbO}_3$  powders with various structures and morphology is believed to be successful and significant.

**3.3. Nonlinear Optical Properties** The second harmonic generation (SHG) intensities of the  $\text{KNbO}_3$  powders prepared in supercritical water are listed in Table 1. Urea is used as the reference material. The  $\text{KNbO}_3$  powder prepared by solid-state method has the strongest SHG intensity. In the hydrothermally prepared samples, sample 8 exhibits the highest SHG intensity, which is almost two times as high as that of urea. It is found that the longer the reaction time of the hydrothermal treatment lasts, the stronger the SHG intensity is.

When the hydrothermally prepared  $\text{KNbO}_3$  powders are further heated at 1000 °C for 2 h, the values of SHG intensity largely increase. All of the  $\text{KNbO}_3$  powders after heating treatment show orthorhombic structures according to XRD characterization. This structure change explains the

dramatic increasing of SHG intensity for samples 4 and 5 before and after heating. On the other hand, the high temperature heating improves the crystallinity for the  $\text{KNbO}_3$  powders, and results in the increasing of SHG intensity.

Table 1. SHG intensities of  $\text{KNbO}_3$  powders compared with urea.

Sample No.	Experimental conditions		SHG Intensities	
			$I(2\omega)_{\text{KNbO}_3} / I(2\omega)_{\text{urea}}$	
	KOH/ M	Time/ hour	Before heating	After heating
Nb-S	Solid-state method		3.17	10.34
8	0.5	24	1.97	9.00
7	0.5	8	0.52	8.14
6	0.5	2	0.31	7.79
5	0.25	24	0.24	5.83
4	0.25	8	0.23	4.31

#### 4. Conclusions

We have demonstrated that the hydrothermal synthesis of  $\text{KNbO}_3$  powders is achieved in supercritical water with low alkalinity. In supercritical water conditions, the KOH concentration needed in the preparation is far lower than those reported before. The obtained particles have rhombohedra and orthorhombic structures due to the alkaline concentration used in the preparation. The orthorhombic  $\text{KNbO}_3$  powders exhibit a strong SHG intensity. As a result, the application of supercritical water for material synthesis is proved to be very successful in improving hydrothermal preparation method.

#### References

- [1] R. J. Reeves, M. G. Jani, B. Jassemnejad, R. C. Powell and G. J. Mizell, W. Fay, *Phys. Rev. B.*, **43**, 71 (1991).
- [2] M. Zgonik, R. Schlessler, I. Biaggio, E. Voit, J. Tscherry and P. Günter, *J. Appl. Phys.*, **74**, 1287 (1993).
- [3] M. Zgonik, K. Nakagawa and P. Günter, *J. Opt. Soc. Am. B.*, **12**, 1416 (1995).
- [4] J. C. Baumert, C. Walther, P. Buchmann, H. Kaufmann, H. Melchior and P. Gunter, *Appl. Phys. Lett.*, **46**, 1018 (1985).
- [5] D. Kip, *Appl. Phys. B.*, **67**, 131 (1998).
- [6] U. Flückiger, H. Arend and H. R. Oswald, *Am. Ceram. Soc. Bull.*, **56**, 575 (1977).
- [7] S. Komarneni, R. Roy and Q. H. Li, *Mater. Res.*

- Bull.*, **27**, 1393 (1992).
- [8] C. H. Lu, S. Y. Lo and H. C. Lin, *Mater. Lett.*, **34**, 172 (1998).
- [9] G. K. L. Goh, F. F. Lange, S. M. Haile and C. G. Levi, *J. Mater. Res.*, **18**, 338 (2003).
- [10] J. F. Liu, X. L. Li and Y. D. Li, *J. Nanosci. Nanotech.*, **2**, 617 (2002).
- [11] J. F. Liu, X. L. Li and Y. D. Li, *J. Cryst. Growth.*, **247**, 419 (2003).
- [12] C. H. Lu, S. Y. Lo and Y. L. Wang, *Mater. Lett.*, **55**, 121 (2002).
- [13] H. Hayashi and K. Torii, *J. Mater. Chem.*, **12**, 3671 (2002).
- [14] Y. Hakuta, K. Seino, H. Ura, T. Adschiri, H. Takizawa and K. Arai, *J. Mater. Chem.*, **9**, 2671 (1999).
- [15] S. K. Kurtz and T. T. Perry, *J. Appl. Phys.*, **39**, 3798 (1968).
- [16] W. T. Wofford, P. C. Dell'Orco and E. F. Gloyna, *J. Chem. Eng. Data.*, **40**, 968 (1995).
- [17] P. G. Jessop, W. Leitner, *Chemical synthesis using supercritical fluids*, (Wiley-VCH, Weinheim, Germany, 1999) p.37.