March 1998

ELSEVIER

Materials Letters 34 (1998) 172–176

MATERIALS LETTERS

Hydrothermal synthesis of nonlinear optical potassium niobate ceramic powder

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Received 16 April 1997; revised 26 May 1997; accepted 30 May 1997

Abstract

Potassium niobate $KNbO_3$ particles having nonlinear optical properties were successfully prepared via a hydrothermal process. When KOH, with a concentration of 8 M, reacted with Nb_2O_5 particles at 200°C, monophasic $KNbO_3$ was obtained. The high concentration of KOH was found to be a critical requisite for the formation of $KNbO_3$. Compared with the traditional solid-state reaction, the hydrothermal process significantly lowered the temperature required for synthesizing $KNbO_3$. The added amounts of Nb_2O_5 in the hydrothermal reaction greatly influenced the morphology and particle size of $KNbO_3$, as well as the intensity of the second harmonic generation. © 1998 Elsevier Science B.V.

PACS: 77.84.-s; 77.84.Dy; 78.20.-e; 81.20. – n
Keywords: Synthesis; Hydrothermal; $KNbO_3$; Powder; Nonlinear optical properties; Second harmonic generation; Electro-optic; Ferroelectric

1. Introduction

In general, the fundamental synthesis processes for ceramics basically use heat treatment for the reactions of mixed raw materials. The reaction rate of these kinds of processes is limited by diffusion among solid particles. In order to enhance the diffusivity, heating at elevated temperatures is generally necessary. However, the high-temperature heating not only is energy-consuming, but also causes unfavorable grain growth of particles of the reaction product. Furthermore, it inevitably results in the evaporation of volatile species, leading to stoichiometric deviation in the composition of the final product. For improving the drawbacks in the conventional solid-state reaction, different kinds of solution processes for synthesis have been extensively investigated. Among these methods, the hydrothermal process has been confirmed to be an efficient method in reducing the synthesis temperatures of ceramics. Furthermore, through this process, the powders with a controlled morphology and chemical composition can be successfully obtained [1–6].

Potassium niobate ($KNbO_3$) is a ferroelectric material having high electro-optic and nonlinear optical coefficients. This material attracts great interest for

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PII S0167-577X(97)00170-5

applications in optical waveguides, frequency doublers and holographic storage systems [7,8]. In the solid-state reaction, 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 calcination temperature has to be higher than 600°C [10,11]. In order to reduce the synthesis temperatures of $KNbO_3$, the hydrothermal process was adopted in this study. The conditions for obtaining $KNbO_3$ in the hydrothermal reaction were first determined. The effects of the amounts of raw materials added for the reaction on the morphology and particle size of $KNbO_3$ powders were determined. The nonlinear optical properties of obtained powders were also measured.

2. Experimental

Reagent grade potassium hydroxide and niobium oxide were used as raw materials. Potassium hydroxide was dissolved in distilled water and mixed with various amounts of Nb_2O_5. Then the mixed slurries were introduced into a teflon-lined autoclave apparatus, and heated at 200 and 250°C for 2–11 h. During the hydrothermal reaction, a mechanical stirrer was used and the rotation speed was 200 rpm. After the hydrothermal reaction, the obtained powders were washed and dried. The compounds present in the powders were identified via X-ray powder diffraction (XRD). The microstructural evolution and the particle size of the samples were examined via scanning electron microscopy (SEM). The second harmonic generation (SHG) response of the powders was measured in the reflection mode using the Kurtz powder method [12]. A Q-switch pulsed Nd:YAG laser operating at 1064 nm with a repetition rate 20 Hz and a pulse width of 6–8 ns was used as the source of radiation. The average incident power used before focusing on the powders was 10–20 mW. The SHG signals were detected by a photomultiplier connected to an oscilloscope. The SHG intensity of the samples compared with that of the reference was used to determine the capability of the second order nonlinear optical effects [13]. Urea was used as the reference material in this study.

3. Results and discussion

Potassium hydroxide was reacted with Nb_2O_5 under various hydrothermal conditions and the compounds formed in the obtained products are summarized in Table 1. The products, determined by X-ray diffraction analysis, are classified into four categories (A to D). At a low concentration of KOH (ranging from 0.04 to 0.25 M), even with the reaction temperature was increased to 250°C and the reaction time prolonged to 11 h, only Nb_2O_5 existed in the products. This result implies that no reaction occurred under these conditions. When [KOH] was increased to 4 M, after the hydrothermal reaction at 200°C, all Nb_2O_5 was dissolved in the solution; however, no precipitates were formed. For [KOH] equal to 6 M, a small amount of $KNbO_3$ was crystallized after the 200°C-reaction. When [KOH] was increased to 8 M, a large amount of $KNbO_3$ was generated. The above results reveal that the concentration of KOH is a critical controlling factor for synthesizing $KNbO_3$. At a low concentration of KOH, Nb_2O_5 could not react with KOH. When the concentration of KOH was increased, Nb_2O_5 could be dissolved in KOH and reacted with KOH. Raising the concentration of KOH tends to increase the solubility of Nb_2O_5 in water and thereby increases the formation of $KNbO_3$.

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 calcining at 500°C and the formation of $KNbO_3$ became nearly complete at 650°C. Although the same raw materials were used in both solid-state and hydrothermal processes, the reactivity of materials in solid form was apparently inferior to that in solution state. Compared with the solid-state reaction, sol–gel [10] and precipitation processes [11], it is confirmed that the hydrothermal process did significantly reduce the synthesis temperature for obtaining pure $KNbO_3$ powders.

As listed in Table 1, when [KOH] was fixed at 8 M, the amounts of Nb_2O_5 were accordingly adjusted to be 0.33, 1.66 and 3.32 g, respectively. Since the total volume of reactants was set at 125 ml, when Nb_2O_5 was completely dissolved during the hy-

Table 1
Products formed in the hydrothermal reaction between KOH and Nb_2O_5 at various conditions

Run No.	Concentration of KOH (M)	Weight of Nb_2O_5 (g)	Reaction temperature (°C)	Reaction time (h)	Products
1	0.02	0.53	200	2	A
2	0.02	0.53	250	2	A
3	0.04	1.05	250	2	A
4	0.25	1.32	220	6	A
5	0.25	1.32	200	11	A
6	4	0.33	200	2	B
7	4	3.32	200	2	B
8	6	0.33	200	2	C
9	6	3.32	200	2	C
10	8	0.33	200	2	D
11	8	1.66	200	2	D
12	8	3.32	200	2	D

A: Nb_2O_5, B: no precipitates, C: a small amount of $KNbO_3$ and D: a large amount of $KNbO_3$.

drothermal reaction, the corresponding concentrations of niobium cations were 0.01, 0.05 and 0.1 M, respectively. Under these three 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. 1. As shown in Fig. 1, no Nb_2O_5 remained in the products. All diffraction peaks were attributed to $KNbO_3$. KN-3 exhibited a pseudocubic structure. The XRD pattern of this powder was consistent with that reported in JCPDS No. 8-212. As for KN-1 and KN-2, because of the split of the diffraction peaks (220) and (002), these two samples showed an orthorhombic structure. The above results imply that the addition amounts of Nb_2O_5 in the hydrothermal reaction influenced the crystalline structure of $KNbO_3$. For further investigation of the phase transformation of KN-3, this sample was heated at elevated temperatures. After heating at 800°C, the (220) and (002) peaks began to split, indicating that the structure of KN-3 transformed from a pseudocubic type into an orthorhombic one. At 1000°C the orthorhombic structure of KN-3 was further developed (Fig. 2).

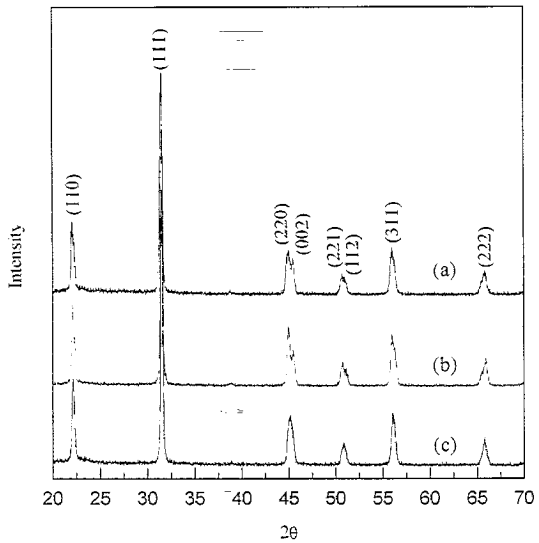

Fig. 1. X-ray diffraction patterns of hydrothermally obtained $KNbO_3$ powders. (a) KN-1, (b) KN-2 and (c) KN-3.

The microstructures of the as-prepared KN-1, KN-2 and KN-3 materials are shown in Fig. 3. Fig. 3 indicates that ultrafine particles of $KNbO_3$ were obtained in the hydrothermal process and their morphology depended on the amounts of Nb_2O_5 used. The particles of KN-1 exhibited an elongated morphology with a high aspect ratio. In the KN-2 material the aspect ratio of particles decreased. As for KN-3, the morphology of the particles became equal-axial and the particle size was around 0.5 μm. When KN-1, KN-2 and KN-3 were further heated at 1000°C, their microstructures greatly varied. As shown in Fig. 3, these three samples experienced different grain growth behavior. The particle sizes of KN-1, KN-2, and KN-3 increased to 1–2, 2–3 and 2–4 μm, respectively.

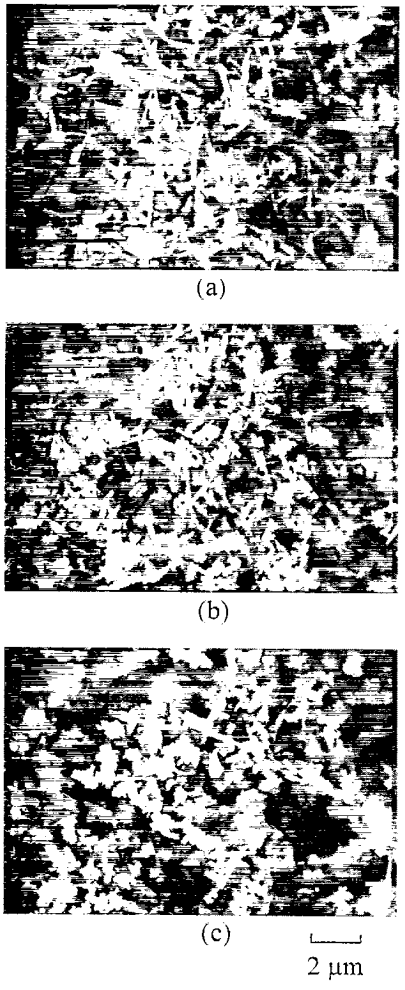

Fig. 2. Scanning electron micrographs of hydrothermally obtained $KNbO_3$ powders. (a) KN-1, (b) KN-2 and (c) KN-3.

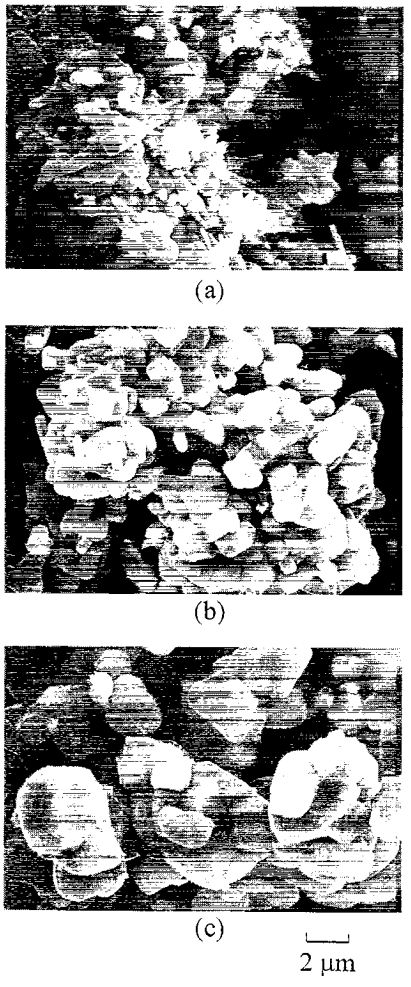

Fig. 3. Scanning electron micrographs of the 1000°C-heated $KNbO_3$ powders. (a) KN-1, (b) KN-2 and (c) KN-3.

The SHG intensities of the $KNbO_3$ powders compared with that of urea are listed in Table 2. For both the as-prepared and 1000°C-heated $KNbO_3$ powders, the magnitudes of the SHG intensity followed the sequence: KN-3 > KN-2 > KN-1. This result indicates that using more Nb_2O_5 in the hydrothermal reaction resulted in the formation of $KNbO_3$ powders having a higher SHG intensity and stronger second order nonlinear optical capabilities. Table 2 also indicates that 1000°C-heating had a positive effect on enhancing the SHG intensity. For a powder having a particle size much less than the characteristic SHG interaction length, the SHG intensity is positively proportional to its particle size [14]. Therefore, when the $KNbO_3$ powders became coarsened at

Table 2
Second harmonic intensity ($I(2\omega)_{sample}/I(2\omega)_{urea}$) of $KNbO_3$ powder

Sample	SHG intensity of as-prepared powders	SHG intensity of 1000°C-heated powders
KN-1	1.67	2.72
KN-2	1.11	1.31
KN-3	0.50	1.03

1000°C, the SHG intensities also increased in all three powders.

4. Conclusion

(i) Using the hydrothermal process we successfully prepared monophasic $KNbO_3$ powders. The synthesis temperature was as low as 200°C. The concentration of KOH in the reaction played an important role in synthesizing $KNbO_3$.

(ii) For the traditional solid-state reaction, the heating temperature for the nearly complete formation of $KNbO_3$ has to be as high as 650°C. Using the hydrothermal process effectively reduced the synthesis temperature of $KNbO_3$.

(iii) The morphology and particle size of $KNbO_3$ powders formed in the hydrothermal reaction depended on the added amounts of Nb_2O_5. The amounts of Nb_2O_5 used also affected the intensity of second harmonic generation of $KNbO_3$.

References

[1] R. Vivekanandan, T.R.N. Kutty, Ceram. Int. 14 (1988) 207.
[2] G.A. Rossetti Jr., D.J. Watson, R.E. Newnham, J.H. Adair, J. Cryst. Growth 116 (1992) 251.
[3] P.K. Dutta, J.R. Gregg, Chem. Mater. 4 (1992) 843.
[4] H. Cheng, J. Ma, B. Zhu, Y. Cui, J. Am. Ceram. Soc. 76 (1993) 625.
[5] C.H. Lu, W.J. Hwang, Mater. Lett. 27 (1996) 229.
[6] C.H. Lu, S.Y. Lo, Mater. Res. Bull. 32 (1997) 371.
[7] P. Gunter, Phys. Rep. 93 (1982) 199.
[8] M.K. Chun, L. Goldberg, J.F. Weller, Appl. Phys. Lett. 53 (1988) 1170.
[9] U. Fluckiger, H. Arend, H.R. Oswald, J. Am. Ceram. Soc. 56 (1977) 575.
[10] M.M. Amni, M.D. Sacks, J. Am. Ceram. Soc. 74 (1991) 53.
[11] K.J. Kim, E. Matijevic, J. Mater. Res. 7 (1992) 912.
[12] S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3789.
[13] S.S.P. Chou, D.J. Sun, H.C. Lin, P.K. Yang, Chem. Commun. 1045 (1996).
[14] G. Bourhill, K. Mansour, K.J. Perry, L. Khundkar, E.T. Sleva, R. Kern, J.W. Perry, I.D. Williams, S.K. Kurtz, Chem. Mater. 5 (1993) 802.