

Study on Microwave-assisted Hydrothermal Synthesis and the Properties of KNbO_3 Powders

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Abstract: KNbO_3 powders with different phases and morphologies were successfully synthesized through the reaction between KOH and Nb_2O_5 by microwave-assisted hydrothermal method at 200°C . Pure KNbO_3 crystals were obtained when the concentration of KOH was maintained from 10mol/L to 14mol/L. According to the XRD, FESEM and TEM characterizations, it could be observed that as increasing the concentration of KOH from 10mol/L to 15mol/L, the KNbO_3 phases changed from rhombohedral to orthorhombic then to tetragonal, and the corresponding morphology of the KNbO_3 powders changed from pyramid-like to rod-like then to cubic-like. Some Nb_2O_5 phases were found when the concentration of KOH increased to 15mol/L. KNbO_3 ceramics were sintered from the KNbO_3 powders by conventional processing. The piezoelectric properties such as the piezoelectric constant d_{33} , the relative permittivity ϵ_{33}/ϵ_0 , the dielectric loss $\tan\delta$, the electromechanical coupling factors k_p and the mechanical quality factor Q_m of the sintered KNbO_3 ceramics were 80 pC/N, 302, 0.023, 0.17, 70, respectively. The tetragonal to orthorhombic and cubic to tetragonal phase transitions temperatures were 223°C and 420°C , respectively.

Key words: KNbO_3 ; microwave-assisted hydrothermal synthesis; piezoelectric; dielectric

KNbO_3 has a large electrooptic coefficient, high nonlinear optical coefficient, and excellent photorefractive characteristic^[1] that make it a very promising candidate in optical applications, such as optical waveguides, frequency doublers^[2], intensity modulators^[3], optical switching and modifiable interconnections^[3], and holographic storage systems^[4]. KNbO_3 has recently attracted much attention from the community of scientists.

KNbO_3 is a perovskite-structured material with ferroelectricity at the temperature below 435°C , which has a great similarity with BaTiO_3 phase transitions. The synthesis of this material faces some difficulties when it is carried out *via* normal solidstate reactions, because sintering at high temperatures often leads to deviate from stoichiometry of the composition of the final products. Over the last years, hydrothermal synthesis has been confirmed to be an efficient method in controlling the morphology and chemical composition of KNbO_3 powders at significantly low temperatures^[5-12].

The combination of microwave and hydrothermal techniques has been used to dissolve all kinds of powders rap-

idly for chemical analysis^[5] in the last few years. Inorganic/organic materials have been synthesized using electronic and magnetic fields in regular motion to produce an electromagnetic wave (2.45 GHz, 12.2 cm microwave) that makes polar molecules absorbing a great quantity of microwave energy^[13]. Energy dissipates in the form of heat from internal resistance to the rotation of the molecular dipoles, resulting in the advantages of uniform heating which makes it simple to produce homogeneous nucleation. Other main advantages of microwave-assisted hydrothermal processing over conventional hydrothermal processing are (i) rapid heating, (ii) faster kinetics, (iii) phase purity with better yield, (iv) higher reproducibility^[14]. Furthermore, it is also possible to produce powders with morphologies that differ from those obtained by conventional hydrothermal methods^[15].

1 Experimental

The reaction between KOH (>82%) and Nb_2O_5 (high-purity, Sinopharm Chemical Reagent Co., Ltd) was

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carried out in a Teflon vessel model (100cm^{-3} capacity) and in a microwave furnace (SineO. MDS-8) operating at 2.45GHz , with an output power of 700W . Firstly, 1.33g of Nb_2O_5 powders were added to 50mL of KOH solution with different concentrations, ranging from 1mol/L to 15mol/L . Then the mixed slurries were transferred into Teflon vessels and placed inside the microwave furnace. The reaction was carried out at 200°C for 60min at the heating rate of $10^\circ\text{C}/\text{min}$. When the temperature reached 200°C , the corresponding pressure inside the Teflon vessel increased to 1.0MPa . The resultant deposition was centrifuged and washed by water and ethanol in sequence thoroughly. After drying in desiccator at 80°C for 8h , the powders were collected for characterizations. Additionally, powders were also prepared for comparison by traditional hydrothermal method at 200°C for 24h with the KOH concentration of 8mol/L . The ceramics were prepared by conventional processing using the as-prepared KNbO_3 powders as raw material. The powders were dried for 10min at 150°C firstly, then 0.2g of the powders was molded into disk-shaped pellet of about 8mm diameter. The pellet was then sintered at 975°C for 2h in air with a heating rate of $3^\circ\text{C}/\text{min}$. To measure the electrical properties, silver paste was painted on both sides of the pellets to form electrodes, and then sintered at 600°C for 2h . After that, the samples were poled under 30 kV/cm DC field at 120°C in silicone oil bath for 20min .

Phases identification of the samples were determined by X-ray diffraction (XRD, Rigaku). The size and morphology of the powders were examined with a field emission scanning electron microscope (FESEM, JSM 6700F). The microstructure and selected area electron diffraction (ED) patterns of the powders were performed with JEM-3010 High-Resolution Transmission Electron Microscope (HRTEM). The piezoelectric constant d_{33} was measured by means of quasistatic d_{33} meter (ZJ-4AN). The dielectric and piezoelectric properties were measured by an Agilent E4980A precision impedance analyzer.

2 Results and discussion

2.1 XRD results

When the concentration of KOH was below 9mol/L , little deposition was obtained. This was mainly because some non-stoichiometric potassium niobate was formed, which was prone to dissolve into water. When increasing the concentration of KOH , more powders could be obtained. From the XRD patterns shown in Fig.1 and Fig.2,

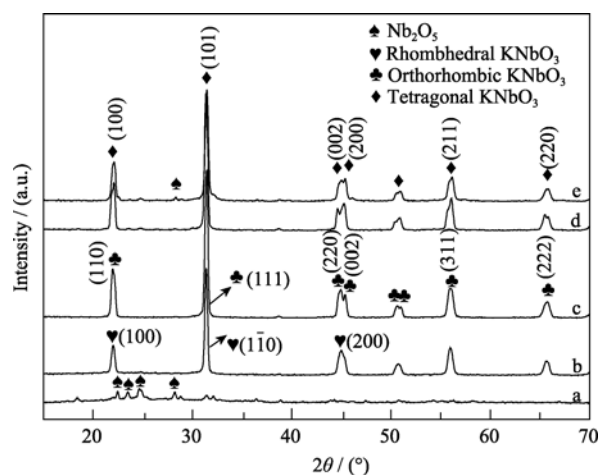


Fig. 1 XRD patterns of the products prepared with different concentrations of KOH

(a) 9mol/L ; (b) 10mol/L ; (c) 11mol/L ; (d) 13mol/L ; (e) 15mol/L

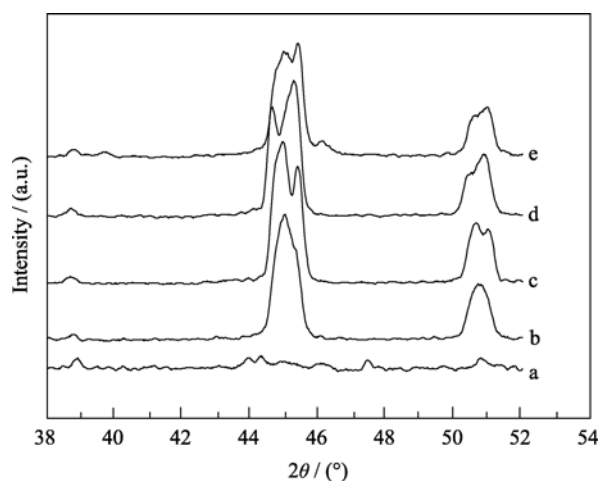


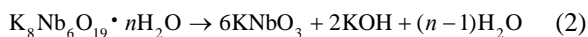
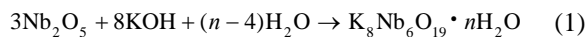
Fig. 2 Enlarged XRD patterns of Fig. 1 at the 2θ range of 40° – 52°

(a) 9mol/L ; (b) 10mol/L ; (c) 11mol/L ; (d) 13mol/L ; (e) 15mol/L

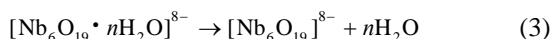
three structure types can be distinguished by the diffraction peaks at 20° – 45° ^[8]. When the concentration of KOH was 9mol/L , the composition of the product was identified to be a mixture of KNbO_3 and Nb_2O_5 . A little amount of KNbO_3 was formed and some undissolved Nb_2O_5 was either existed. As increasing the concentration of KOH to 10mol/L , rhombohedral KNbO_3 phase (JCPDS71-0947) was formed in the reaction. When the concentration of KOH changed to 11mol/L , the obtained product could be indexed to the orthorhombic phase (JCPDS 32-0822). The clearly split peaks could be indexed to (220) and (002) peaks of the orthorhombic phase^[8]. The peak intensity of the lattice plane (002) increased continuously as the concentration of KOH was increased to 13mol/L as shown in Fig.1d, resulting in the phase transition to the tetragonal phase (JCPDS 71-0948), while the broad peaks near 45° whose intensity was reversed when compared with orthorhombic ones were considered to correspond to (002) and (200) for the tetragonal ones^[8]. When the concentration of KOH was increased to 15mol/L , the peak of the lattice

plane (200) decreased to the equivalent to the lattice plane (002), as shown in Fig.1e. Some impurity appeared when the concentration of KOH was increased to 15mol/L, which could be indexed to Nb_2O_5 .

KOH concentration was believed to be the key to determine the crystal phase of KNbO_3 . The reaction mechanism was as follows:



The reaction (2) could be divided into two parts:



When the KOH concentration was below 10mol/L, the reaction was followed by reaction (1). Some soluble material $\text{K}_2\text{Nb}_8\text{O}_{21}$ was formed. When the KOH reached more than 10mol/L, the reaction was dominated by reaction (2), insoluble KNbO_3 crystal formed initially. However, when the KOH concentration was too high, the reaction (4) was restrained because of the high OH^- concentration, as a result, some non-reacted Nb_2O_5 was detected in the XRD result.

2.2 FESEM images

The FESEM images of the powders obtained from the reactions with different concentrations of KOH were shown in Fig.3. Figure 3(a) shows the morphology of the sample with the KOH concentration of 9mol/L. Some immature particles with irregular shapes were formed. After increasing the concentration of KOH to 10mol/L, it was observed that pyramidal KNbO_3 crystals with height of $1\mu\text{m}$ were formed (Fig.3(b)). And the pyramidal KNbO_3 crystal was constructed by superimposed sheet-like layers. Referring to the XRD pattern in Fig.1b, it could be inferred that the sheet structure was formed due to the grain growth along the lattice plane (200). The formation of this superimposed structure followed the BCF theory^[16]. The morphology of the powders obtained with the concentration of KOH of 11mol/L could be regarded as a superimposed construction of square layers, and some individual cubic-shaped particles occurred as well (Fig.3(c)). According to the comparison with Fig.3(b), the change of the morphology was due to the growth of the lattice plane (002). Rod-like crystals with the length of about $1\mu\text{m}$ and the diameter of about 300nm were presented in Fig.2(d), which corresponded to the powders obtained with the concentration of KOH of 13mol/L. According to the combination of XRD and SEM results, it could be concluded that the continuous growth along the lattice plane (200) of the tetragonal phase made contribution to this rod-like morphology. At the same time, a small amount of cubic-like crystals were also observed in

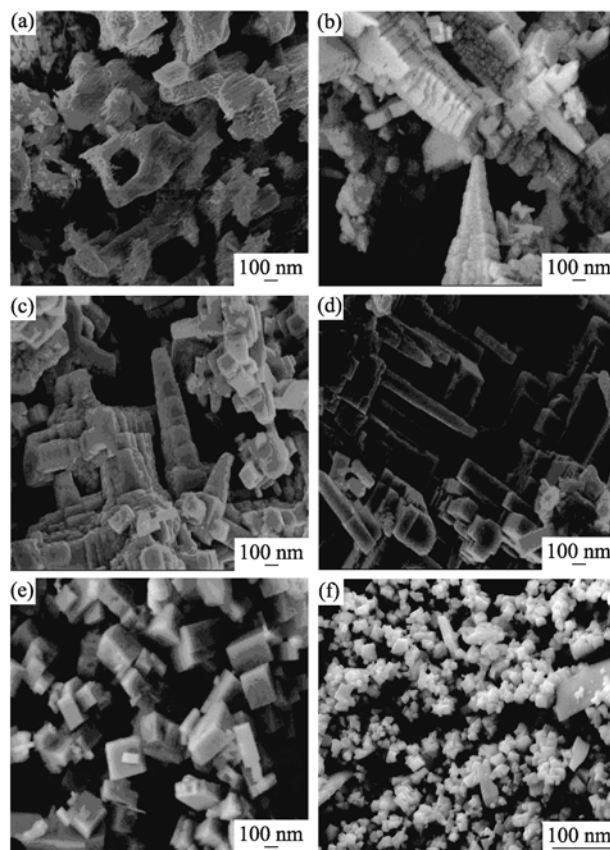


Fig. 3 FESEM images of powders obtained at different concentrations of KOH

(a) 9mol/L; (b) 10mol/L; (c) 11mol/L; (d) 13mol/L; (e) 15mol/L; (f) Powders prepared under traditional hydrothermal method at 220°C for 24h with the KOH concentration of 8mol/L

Fig.3(d), which showed the transition state from the rod-like crystals to the cubic-like crystals. Well-crystallized cubic-like crystals with the particle size of about 500nm were formed in the powders obtained with the concentration of KOH of 15mol/L (Fig.3(e)). Fig. 3(f) shows the SEM images of powders prepared by traditional hydrothermal method under the optimum conditions (at 220°C for 24h with the KOH concentration of 8mol/L) which was suggested in our previous work. Compared with the microwave-assisted hydrothermal method, the particle size of the powders prepared by traditional hydrothermal method was much smaller (about 20nm). Furthermore, higher temperature and longer reaction time were required by traditional hydrothermal method compared with microwave-assisted hydrothermal method.

Microwave could be absorbed by some polar molecules with high dielectric loss, such as water molecules. Permanent dipole moment of water molecules were forced to change orientation rapidly, resulting in rapid 'internal heating'. From the comparison of microwave-assisted hydrothermal and traditional hydrothermal method, it could be inferred that this rapid 'internal heating' of

microwave-assisted hydrothermal method could evidently reduce the reaction time of crystal nucleation and growth and increase the particle size of KNbO₃ crystal.

2.3 TEM images and ED patterns

Figure 4 shows the TEM images and selected area electron diffraction (SAED) pattern of the KNbO₃ powders obtained when the concentration of KOH equals to 11mol/L. It could be confirmed that the pyramidal structure was formed according to epitaxial growth along the lattice plane (002), which were fully consistent with the XRD results. Figure 4(c)^[17] shows different stages of the pyramid-like crystal growth. In this model, the KNbO₃ crystal grew from supersaturated solution. Then the ions were absorbed at the step site through the diffusion process. The previous layer acted as substrates or base surfaces for the nucleation and epitaxial growth along [002] of the next layer. As shown in the TEM image, the layer size decreases in a stepped way with random step heights towards the pyramid tip.

2.4 Piezoelectric and dielectric properties

Little amount of precipitation could be obtained when the KOH concentration was below 12mol/L, because the OH⁻ was not high enough to convert soluble K₂Nb₈O₂₁•nH₂O into insoluble KNbO₃. The sample with the concentration of KOH of 13mol/L was prepared into ceramics by traditional process. The piezoelectric properties of the KNbO₃ ceramics (measured at 1kHz at room temperature) were shown in Table 1. The *d*₃₃ was reached 80 pC/N, which was equivalent to the reported *d*₃₃ of K_{0.5}Na_{0.5}NbO₃^[18].

The relative permittivity vs temperature data was recorded at frequencies from 10² to 10⁶ Hz, which was shown in Fig.5. The material possessed two maximums in

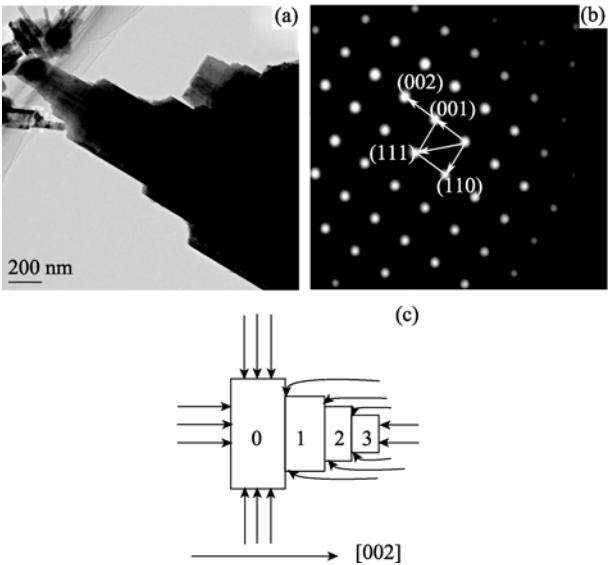


Fig. 4 TEM image (a) and SAED pattern (b) of powders obtained with KOH=11mol/L and sketch showing (c) of pyramid-like crystal growth

Table 1 Piezoelectric properties of the KNbO₃ ceramics prepared from sample with the concentration of KOH of 13mol/L

Parameters	ϵ_{33}/ϵ_0	$d_{33}/(\text{pC}\cdot\text{N}^{-1})$	$\tan\delta$	k_p	Q_m
Values	302	302	0.023	0.17	70

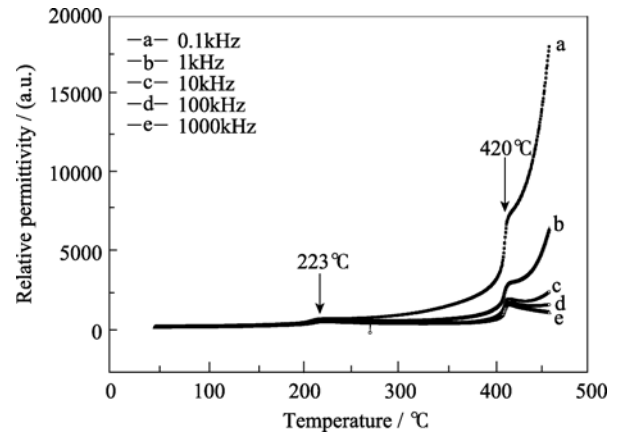


Fig. 5 Temperature dependence of relative permittivity for the KNbO₃ ceramics

dielectric values around 223°C and 420°C, each representing the tetragonal to orthorhombic and cubic to tetragonal phase transitions, respectively. Low frequency dispersion could be observed above 200°C and it might be related to hygroscopic sensitivity of the materials^[19].

3 Conclusion

Pure KNbO₃ crystal was successfully synthesized through the reaction between KOH and Nb₂O₅ by a microwave-assisted hydrothermal method at 200°C. The concentration of KOH was a critical factor to control the synthesis of KNbO₃. When the concentrations of KOH were in the range of 10–14mol/L, the KNbO₃ phase changed from rhombohedral, orthorhombic to tetragonal. Little Nb₂O₅ reformed when 15mol/L KOH was used. Morphology of the powders obtained with the concentration of KOH of 10–15mol/L changed from pyramid-like, rod-like to cubic-like, which corresponded to the change in the growth of the lattice plane (002) of the orthorhombic phase. The piezoelectric properties of KNbO₃ ceramics such as the piezoelectric constant *d*₃₃, the relative permittivity ϵ_{33}/ϵ_0 , the dielectric loss $\tan\delta$, the electromechanical coupling factors *k_p* and the mechanical quality factor *Q_m* of the sintered KNbO₃ ceramics were 80 pC/N, 302, 0.023, 0.17, 70, respectively. The tetragonal to orthorhombic and cubic to tetragonal phase transitions temperatures were 223°C and 420°C, respectively.

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微波水热法制备 KNbO_3 粉体及其性能研究

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摘 要: 以氢氧化钾(KOH)和五氧化二铌(Nb_2O_5)为原料, 通过微波水热法在 200°C 下合成出具有不同晶相、形貌的铌酸钾粉体(KNbO_3)。当 KOH 浓度在 $10\sim 14\text{mol/L}$ 时, 可以制备出纯相的 KNbO_3 粉体。X 射线衍射(XRD)、场发射扫描电镜(FESEM)和透射电镜(TEM)分析可知, KOH 浓度由 10mol/L 增大到 15mol/L 时, KNbO_3 粉体由斜方六面体变为正交相, 再转变为四方相, 对应的形貌也由金字塔状变为棒状, 再转变为立方状。当 KOH 浓度增大到 15mol/L 时, 出现了 Nb_2O_5 杂相。常压烧结制备了 KNbO_3 陶瓷, 其介电常数达到 302, 介电损耗为 0.023, 压电常数达到 80pC/N , 平面机电耦合系数为 0.17, 机械品质因数为 70, 居里温度为 420°C , 正交-四方相变温度为 223°C 。

关 键 词: 铌酸钾; 微波水热; 压电性能; 介电性能

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