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Low-temperature synthesis of $ZnNb_2O_6$ powders via hydrothermal method

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Abstract

$ZnNb_2O_6$ powder was successfully synthesized via hydrothermal method with Nb_2O_5 and $Zn(NO_3)_2{\cdot}6H_2O$ as raw materials and cyclohexane as solvent. Phase composition, morphology, and chemical composition were determined via a combination of XRD, SEM, TEM and EDS techniques. The effects of synthesis temperature and reaction time on phase composition and particle morphology were investigated in this paper. The results showed that fine $ZnNb_2O_6$ powders could be obtained at a hydrothermal temperature of 190 °C or above under different reaction time.

Keywords: A. Powders: chemical preparation; B. Composites; B. Microstructure-final; D. Niobates

1. Introduction

Multilayer microwave devices have received much attention due to the rapid progress in satellite and mobile communications such as cellular phones, GPS, etc. [1]. Although much progress has been made with respect to applications of microwave dielectrics, a fundamental understanding of dielectric properties such as permittivity (ε_r), quality factor, temperature coefficient of resonant frequency (τ_f) is still being developed [2]. Recently, the binary niobate such as AB_2O_6 (where A = Ca, Mg, Zn, Co, Ni, Cu, Mn and B = Nb, Ta) are found to be promising candidates for application in microwave devices owing to their excellent dielectric properties such as low loss, high dielectric constant [3–5]. Among these compounds, $ZnNb_2O_6$ is known as excellent microwave dielectric materials, which has excellent dielectric properties: $Q \times f = 87{,}300$ GHz, $\varepsilon_r = 25$ and $\tau_f = 56$ ppm °C [3,6]. Thus, more attention has been paid on this material in the past, especially on the effects of additives on microwave dielectric properties as well as low temperature sintering behavior [7–9] while the powder synthesis is ignored to some extent, though it is quite crucial to the performance of the material.

The $ZnNb_2O_6$ powders prepared by solid-state reaction [10] require high temperature and harsh reaction conditions. The powders prepared by this method are always relatively large in particle size with broad particle size distributions. Then citrate sol–gel method [11] and molten salt method [1] have been developed to synthesize $ZnNb_2O_6$ powders respectively, but high temperature is inevitable. The hydrothermal process has been known to be one of the most important synthetic methods, which can be defined as any heterogeneous reaction in the presence of aqueous solvents or mineralizers under high pressure and temperature conditions to dissolve and recrystallize (recover) materials that are relatively insoluble under ordinary conditions [12]. Meanwhile this method has advantages of low cost, simple process and well-controlled morphology. Therefore, it has been a goal for many researchers to obtain $ZnNb_2O_6$ powders by a hydrothermal process under milder condition in this field. However, to our knowledge, there was no report on the preparation of $ZnNb_2O_6$ via hydrothermal method. In our previous experiments, we tried to obtain $ZnNb_2O_6$ powers using water as solvent under alkaline or acidic conditions by hydrothermal method, but all the efforts were not successful. The past research has shown that the cyclohexane is a good solvent for preparation of nanopowders and nanostructure [13,14]. Therefore, in this study, we try to synthesize $ZnNb_2O_6$ powders via hydrothermal method with Nb_2O_5 and $Zn(NO_3)_2{\cdot}6H_2O$ as raw materials and cyclohexane as solvent.

2. Experimental procedure

Nb_2O_5 and $Zn(NO_3)_2{\cdot}6H_2O$ were used as raw materials and cyclohexane was used as solvent. All the chemicals were

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analytical grade. Mixtures of cyclohexane and raw materials with a molar ratio of Zn to Nb of 0.5 were put in a Teflon-lined autoclave and then were heated to 180 °C, 190 °C and 200 °C, and held for 10 min, 30 min and 60 min, respectively. After that, the autoclave was naturally cooled to room temperature. The product was orderly washed several times with absolute alcohol and deionized water. Then the powders were dried at 60 °C for 12 h.

The phase composition of the as-prepared powders was identified by X-ray diffraction (XRD, Model D8 Advance, Bruker, Germany) using Cu Kα radiation. The morphology of the powders was investigated by transmission electron microscopy (TEM, JEM-2100, Japan). The elemental composition was studied by EDS (INCA Energy, England).

3. Results and discussions

Fig. 1 shows XRD patterns of the powders synthesized via hydrothermal method at 180 °C, 190 °C and 200 °C for 1 h. As seen from Fig. 1, the product prepared with a heat treatment temperature of 180 °C is mainly composed of Nb_2O_5. When the temperature increased to 190 °C, the main phase of the product is $ZnNb_2O_6$ and a small amount of Nb_2O_5. Then the phase composition of product has no obvious changes when the temperature increased from 190 °C to 200 °C. So the crystal $ZnNb_2O_6$ can be successfully obtained at a hydrothermal temperature of 190 °C or above. Note that a temperature of 600 °C was needed for the crystal $ZnNb_2O_6$ powders synthesis through the citrate sol-gol method and molten salt method [1,11]. Thus, the crystal $ZnNb_2O_6$ powders can be obtained by the hydrothermal method in the present study at a temperature which is significantly lower than those by other methods.

Fig. 2 is the XRD pattern of $ZnNb_2O_6$ powders synthesized at 190 °C for 10 min, 30 min and 60 min, respectively. As shown in Fig. 2(a–c), there is no obvious difference in the phase composition of powders synthesized at 190 °C for 10 min, 30 min and 60 min. Fig. 3 shows the XRD patterns of $ZnNb_2O_6$ powders synthesized at 200 °C for 10 min, 60 min and 6 h. We cannot find obvious difference from these results. It suggests that the increase of reaction time neither changes the composition of the powders, nor improves crystallization degree of the powders.

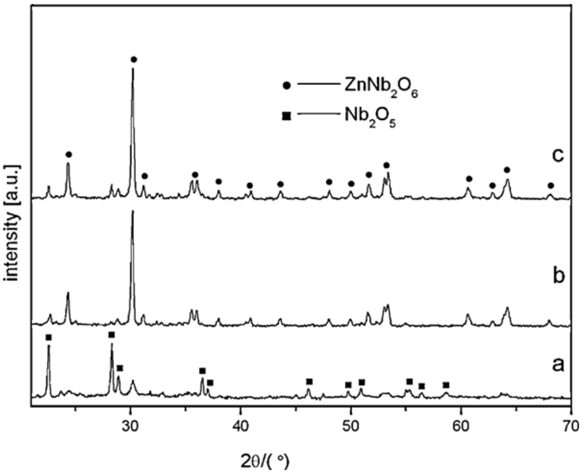

Fig. 1. XRD patterns of the $ZnNb_2O_6$ powders synthesized by hydrothermal method at (a) 180 °C, (b) 190 °C and (c) 200 °C for 1 h.

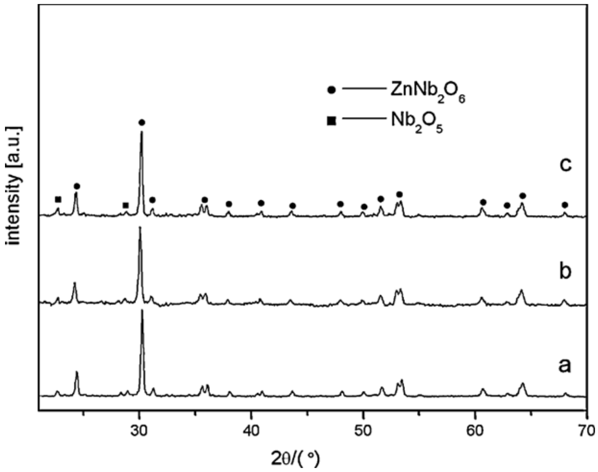

Fig. 2. XRD patterns of powders synthesized at 190 °C for (a) 10 min, (b) 30 min and (c) 60 min.

Fig. 4 shows the TEM photographs of the $ZnNb_2O_6$ powders synthesized at 190 °C for 10 min, 30 min and 60 min. It indicates that the particles of powders obtained under three conditions are equiaxial grains with same morphologies. The particle size is about 50–400 nm. This result further confirms that the increase of the reaction time cannot effect on the grain growth of $ZnNb_2O_6$ powders. The results of EDS analysis indicates that the ratios of Zn to Nb in the powders synthesized at 190 °C for 10 min and 60 min are 1:1.79 and 1:1.87, respectively (shown in Fig. 5(a and b)). These ratios approximately equaled to the ratio of Zn to Nb in $ZnNb_2O_6$ (1:2). Fig. 6 shows TEM and HRTEM images of $ZnNb_2O_6$ powders synthesized at 190 °C for 10 min and 60 min. The lattice fringes with spacing of 0.364 nm (showed in Fig. 6(a)) and 0.298 nm (showed in Fig. 6(b)) can be indexed to the spacing of (0 3 1) and (1 3 1) planes of $ZnNb_2O_6$ (0.3644 nm, 0.2952 nm, PCPDS Card No 37-1371), respectively. These experiments support that $ZnNb_2O_6$ crystallites have been synthesized successfully.

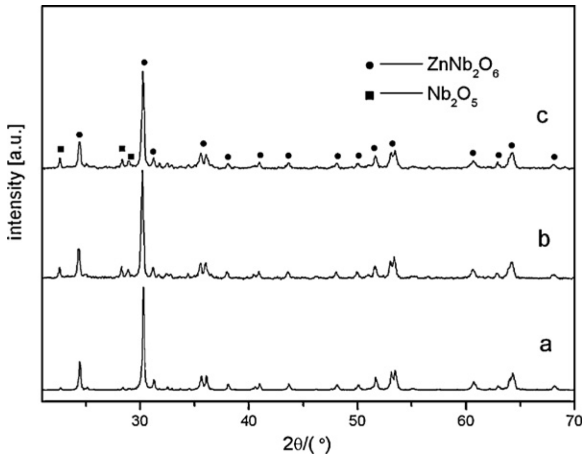

Fig. 3. XRD patterns of powders synthesized at 200 °C for (a) 10 min, (b) 60 min and (c) 6 h.

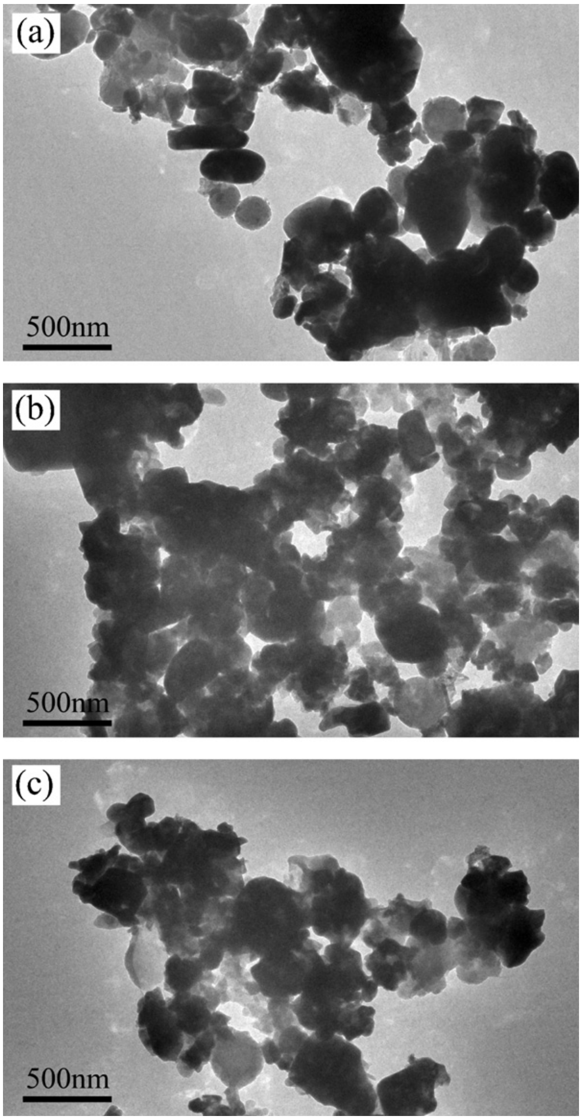

Fig. 4. TEM photographs of products heated at 190 °C for (a) 10 min, (b) 30 min and (c) 60 min.

Based on the above analysis, obviously it is observed that the reaction time has insignificant effect on phase composition and morphology of $ZnNb_2O_6$ powders. In other words, the hydrothermal reaction is very quick and the rapid reaction completes in a short time as soon as it reaches the reaction temperature. It should also be paid attention that the inside surface of teflon-lined autoclave was strongly ablated and a black pit with 1 mm deep was formed on it when the $ZnNb_2O_6$ powders were obtained at 180 °C above. Elements F and C in the $ZnNb_2O_6$ powders was found (Fig. 5). While the inside surface of teflon-lined autoclave was intact when the $ZnNb_2O_6$ powders were not obtained (when the reaction temperature was below 180 °C). Therefore, it is guessed that the hydrothermal reaction may go as follows: zinc nitrate hexahydrate is decomposed into ZnO, NO_2 and O_2 which causes the strong oxidation of PTFE, liberating a large amount of heat under cyclohexane condition, which results in momentary high pressure and temperature. In this condition, the $ZnNb_2O_6$ is rapid obtained from ZnO and Nb_2O_5, and the rapid reaction is

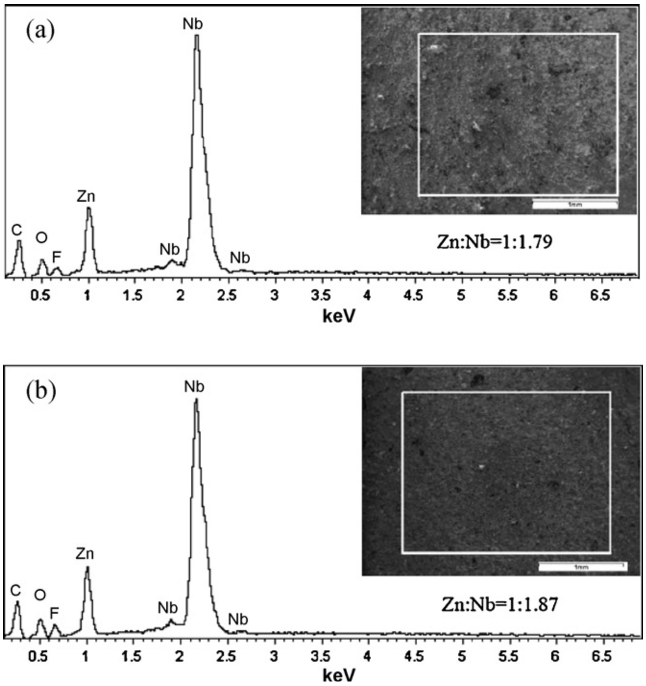

Fig. 5. EDS analysis of $ZnNb_2O_6$ powders synthesized at 190 °C for (a) 10 min and (b) 60 min.

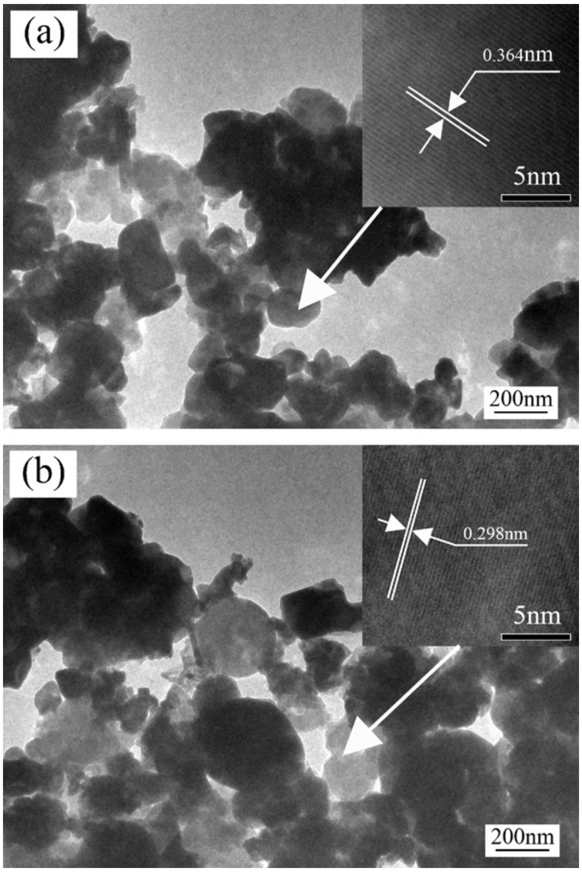

Fig. 6. TEM and HRTEM images of $ZnNb_2O_6$ powders synthesized at 190 °C for (a) 10 min and (b) 60 min.

terminated as soon as oxygen is used up. The residuum of oxidized PTFE was mixed into as-obtained $ZnNb_2O_6$ powders. So the peak of F and C is found in the EDS patterns of the $ZnNb_2O_6$ powders. Because the amount of O_2 from Zinc nitrate is very little, so the condition with high pressure and temperature is only kept instantaneously. Therefore the reaction of ZnO and Nb_2O_5 is not complete, and a little of Nb_2O_5 exists in the $ZnNb_2O_6$ powders.

4. Conclusions

The $ZnNb_2O_6$ powder was successfully synthesized using Nb_2O_5 and $Zn(NO_3)_2{\cdot}6H_2O$ as raw materials and cyclohexane as solvent under hydrothermal conditions in the present study. The lowest hydrothermal synthesis temperature of $ZnNb_2O_6$ powders was 190 °C. The obtained $ZnNb_2O_6$ powders had good crystallinity. The effect of reaction time on phase composition and particle morphology was not obvious.

Acknowledgements

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