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Short communication

Synthesis of $ZnNb_2O_6$ powder with rod-like particle morphologies

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Abstract

A $ZnNb_2O_6$ powder was synthesized through the molten salt method. The XRD and SEM results indicated that the crystal $ZnNb_2O_6$ powder with rod-like particle morphologies could be obtained via this method at temperature of 600 °C, which is significantly lower than that required by solid-state reaction, where a calcining temperature of 800 °C was needed and the obtained $ZnNb_2O_6$ particles were equiaxial. The heat treatment temperature scarcely affected the $ZnNb_2O_6$ particle morphologies in the molten salt synthesis process.

Keywords: $ZnNb_2O_6$ powder; Molten salt method; Particle morphology

1. Introduction

With the continuing proliferation of wireless communications technologies operating at microwave frequencies, there has an ever-increasing demand for high performance dielectric ceramics [1]. $ZnNb_2O_6$ ceramics is known as an excellent microwave dielectric material with dielectric parameters of $Q \times f = 87300$ GHz, $\varepsilon_r = 25$, and $\tau_f = 56$ ppm/°C. Another advantage for this material is its lower fabrication temperature [2,3]. Thus, more and more attentions have been paid on this material in the past and most of them was focused on the effects of additives on microwave dielectric properties [4,5] as well as low temperature sintering behavior [6,7] while the powder synthesis was ignored to some extent, though it is quite crucial to the performance of the material. The $ZnNb_2O_6$ powder synthesis could be performed using the conventional solid-state reaction method [3,4]. The synthesis temperature in this method, however, was quite high. Thus, an alternate route of synthesis at lower temperature was increasingly demanded [8]. The molten salt method is a promising route [9]. The $ZnNb_2O_6$ powder synthesis through this method was quite few in the literature [10].

The aim of this study was to synthesize the $ZnNb_2O_6$ powder through the molten salt method. The $ZnNb_2O_6$ powder synthesis through the conventional solid stat reaction method was also performed for comparison. The obtained $ZnNb_2O_6$ powders were characterized and the results were discussed.

2. Experimental procedure

ZnO and Nb_2O_5 powders with purity higher than 99.0 wt% were used as raw materials. A powder mixture of ZnO and Nb_2O_5 with ZnO content of 50 mol% was prepared as a reactant. An inorganic salt mixture was prepared using KCl–NaCl–$ZnCl_2$ (purity higher than 99.0 wt%) as a solvent and KCl:NaCl:$ZnCl_2$ was 0.45:0.45:0.1 in mol. The prepared reactant and the solvent was mixed at a weight ratio of 1 to 3 and ball milled using Al_2O_3 balls for 2 h in an ethanol medium. After ball milling, the obtained slurry was dried at 60 °C for 12 h to remove the ethanol. Heat treatment was then carried out at a temperature range of 550–800 °C for 2 h in a muffle furnace with a heating speed of 10 °C/min. After heat treatment, the product was washed several times using hot deionized water to remove the residual salt [8]. The product were then dried and its phase composition was identified using an X-ray diffractometer (XRD, Model D8 Advance, Bruker, Germany). The particle morphology observations were performed using a scanning electron microscopy (SEM, Model JSM-5800, JEOL, Japan).

In order to compare these results with those through the conventional solid-state reaction method, the $ZnNb_2O_6$ powder synthesis was also carried out by directly calcining the reactant at 800 °C for 2 h and the obtained product was characterized using the XRD and SEM.

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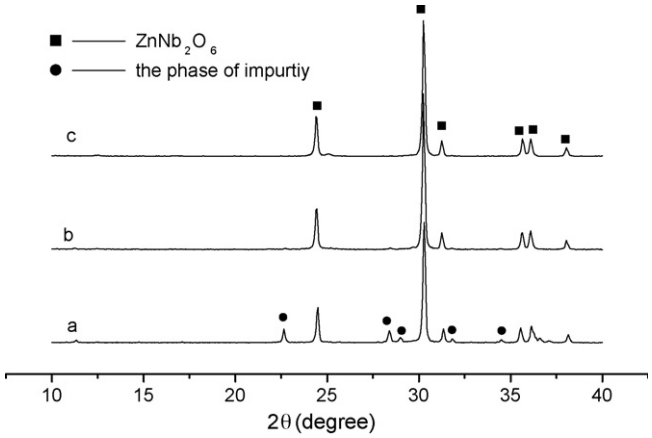

Fig. 1. XRD patterns of the $ZnNb_2O_6$ powders synthesized through molten salt method at temperatures of 575 °C (a), 600 °C (b), and 625 °C (c).

3. Results and discussion

Fig. 1 shows XRD patterns of the $ZnNb_2O_6$ powder synthesized through the molten salt method at different temperatures. As seen from Fig. 1, with a heat treatment temperature of 575 °C some impurity was present in the product. The pure crystal $ZnNb_2O_6$ powder, however, could be successfully obtained at a temperature of 600 °C or its above. Note that a calcining temperature of 800 °C was needed for the crystal $ZnNb_2O_6$ powder synthesis through the conventional solid-state reaction method [4,5]. Thus, the crystal $ZnNb_2O_6$ powder could be obtained in the present study at temperature significantly lower than that through the conventional solid-state reaction method, endowing the powder fabrication process with a promise of lower cost [11].

Fig. 2 shows SEM morphologies of the $ZnNb_2O_6$ powders synthesized through the two methods. As shown in Fig. 2(a), the obtained $ZnNb_2O_6$ particles through the solid-state reaction method were equiaxial with particle diameter of about 0.3 μm. The $ZnNb_2O_6$ particles synthesized through the molten salt method, however, were not equiaxial but rod-like with particle size of 2–3 μm in length and 0.4–0.5 μm in diameter (Fig. 2(b–d)). Note that there has no visible difference of particle morphologies in Fig. 2(b–d), indicating scarcely affect of the heat treatment temperature upon the particle morphologies. Fig. 2 also showed that the obtained $ZnNb_2O_6$ powder through the molten salt method has less agglomeration than that through the conventional solid-state reaction method.

4. Conclusion

The crystal $ZnNb_2O_6$ powder was successfully synthesized through the molten salt method using a KCl–NaCl–$ZnCl_2$ mixture as a solvent. The heat treatment temperature of 600 °C was significantly lower than that through the conventional solid-state reaction method, where a calcining temperature of 800 °C was needed. The obtained $ZnNb_2O_6$ powder was not equiaxial but rod-like. The effect of the heat treatment temperature on the particle morphologies was investigated and no visible difference was observed.

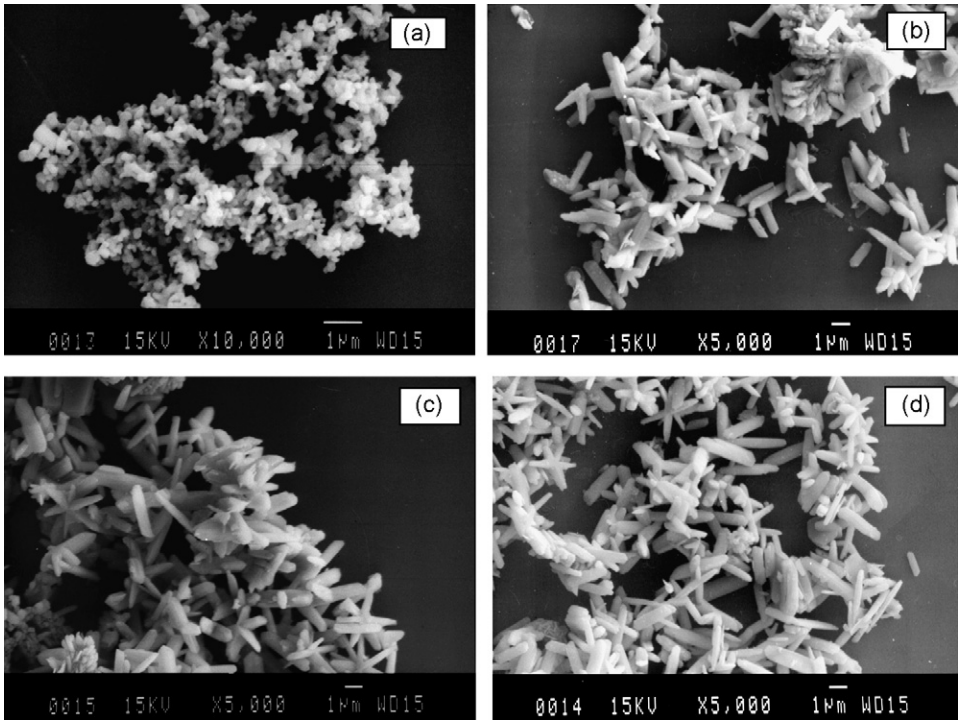

Fig. 2. SEM morphologies of the $ZnNb_2O_6$ powders synthesized through the solid-state reaction method at 800 °C for 2 h (a) and the molten salt method at temperatures of 600 °C (b), 700 °C (c), and 800 °C (d) for 2 h.

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References

[1] R.C. Pullar, K. Okeneme, N.McN. Alford, Temperature compensated niobate microwave ceramics with the columbite structure, $M^{2+}Nb_2O_6$, J. Euro. Ceram. Soc. 23 (2003) 2479.

[2] M. Maeda, T. Yamamura, T. Ikeda, Dielectric characteristics of several complex oxide ceramics at microwave frequencies, Jpn. J. Appl. Phys. Part 1-Suppl. 26 (1987) 76.

[3] H.J. Lee, I.T. Kim, K.S. Hong, Dielectric properties of AB_2O_6 compounds at microwave frequencies (A = Ca, Mg, Mn, Co, Ni, Zn and B = Nb, Ta), Jpn. J. Appl. Phys. Part 2 (1997) 318.

[4] Y.Ch. Zhang, L.T. Li, Effects of additives on microstructures and microwave dielectric properties of $ZnNb_2O_6$ ceramics, Mater. Sci. Eng. B99 (2003) 282.

[5] D.W. Kim, K.H. Ko, K.S. Hong, Influence of copper(II) oxide additions to zinc niobate microwave ceramics on sintering temperature and dielectric properties, J. Am. Ceram. Soc. 84 (6) (2001) 1286.

[6] F.Y. Cheng, Dielectric properties of $(1-x)Bi_2(ZnNb_2)_yO_{3+6y+x}Bi_3(Ni_2Nb)O_9$ ceramics, J. Mater. Sci. Lett. 18 (1999) 521.

[7] F.Y. Man, C.L. Hung, W.R. Warren, Low-firing, temperature-stable dielectric compositions based on bismuth nickel zinc niobates, J. Am. Ceram. Soc. 73 (4) (1990) 1106.

[8] M. Thirumal, P. Jain, A.K. Ganguli, Molten salt synthesis of complex perovskite-related dielectric oxides, Mater. Chem. Phys. 70 (2001) 7.

[9] R.H. Arendt, J.H. Rosolowski, J.W. Szmasek, Mater. Res. Bull. 14 (1979) 703.

[10] M. Thirumal, A.K. Ganguli, Synthesis and dielectric properties of magnesium niobate-magnesium tantalate solid solutions, Mater. Sci. Bull. 13 (2001) 2421–2427.

[11] K. Wada, K. Kakimoto, H. Ohsato, Microstructure and microwave dielectric properties of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ ceramics containing columnar crystals, J. Euro. Ceram. Soc. 23 (2003) 2535.