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Sintering behavior and microwave dielectric properties of nano zinc niobate powder

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Abstract

Nanosized $ZnNb_2O_6$ powders obtained by high energy ball milling (HEBM) and subsequent heat treatment were compacted and sintered into near full density ceramics using pressureless sintering. The prepared ceramic samples were characterized by field emission scanning electron microscopy, X-ray diffraction, and microwave dielectrical property measurements. All samples prepared at sintering temperatures ranging from 975 to 1100 °C, exhibit a single columbite phase and their relative densities range from ~87% to ~99%. The variation trend of permittivity and $Q \times f$ value was in accordance with variation trend of relative density. Pure columbite $ZnNb_2O_6$ ceramic sintered at 1050 °C for 5 h exhibited good microwave dielectric properties with a permittivity about 23.6, $Q \times f$ value about 72,357 GHz, and temperature coefficient of resonant frequency about −67.72 ppm/°C.

Keywords: A. Sintering; Microwave dielectric properties; High energy ball milling; Nanopowder; $ZnNb_2O_6$

1. Introduction

During the past couple of decades, microwave dielectric ceramics were increasingly used for resonators, filters, duplexers, and antennas in systems for wireless communications. Requirements for the microwave dielectric ceramics are that, they should have high *Qf* values with moderate dielectric constant characteristics and near-zero temperature coefficients of resonant frequency. And also, with the development of low-temperature co-fired ceramics (LTCC) technology, low-temperature sinterable materials become more important [1–6]. Although a few of the alkaline-earth based materials such as $Ba(B'_{1/3}B''_{2/3})O_3$ (B': Mg, Zn; B″: Nb, Ta) [7–10] are found to be suitable for dielectric resonator applications, the search for new dielectric materials is in progress to replace existing materials due to the high cost of Ta and higher sintering temperature (> 1500 °C). Series of $A^{2+}B_2^{5+}O_6$ (A=Mg, Zn, Co; B=Nb, Ta) ceramics were first investigated by Maeda et al. [11]. A comprehensive study on the microwave dielectric properties of this family was accomplished by Lee and colleagues [12–19] In particular, the columbite – structured $ZnNb_2O_6$ compound (ε_r (dielectric constant) ~25, $Q \times f$ (product of quality factor and resonant frequency) ~83,700 GHz, and τ_f (temperature coefficient of resonant frequency) ~ −56 ppm/°C) [9], having a high $Q \times f$ and a comparably low sintering temperature, was proposed as a candidate dielectric for high-frequency applications.

Most of the previous reports on the studies on the microwave dielectric properties of $ZnNb_2O_6$ are on the materials synthesized by the ceramic process involving high-temperature solid state reactions. Recently, it has been reported that good microwave dielectric properties can be attained for $ZnNb_2O_6$ by reaction sintering of nano-sized ZnO–Nb_2O_5 powder mixture [20]. So far, there have been no attempts to study the effect of sintering of $ZnNb_2O_6$ compacts derived from nanocrystalline materials at lower temperatures on the microstructure and microwave dielectric characteristics. The advantage of the nanocrystalline powders is that they are more sinterable due to the fine particle nature as well

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as the high surface area [21–25]. In our former work [26], we adopted the high-energy ball-milling method (HEBM) in order to decrease the synthesis temperature for $ZnNb_2O_6$, which was successfully lowered to around 650 °C with nano-sized particles. In the present work, we continued our previous study to elucidate the effect of HEBM, time and sintering temperature on the microstructure and microwave dielectric behaviors of $ZnNb_2O_6$ ceramics prepared by nanopowder.

2. Exprimental procedures

Highly pure powders of ZnO and Nb_2O_5 (all from Sigma Aldrich Co., USA) were mixed in stoichiometric proportions to form $ZnNb_2O_6$. The milling experiment was carried out with high-energy planetary mill. A WC vial with diameter of 80 mm and 60WC balls with diameter of 10 mm were used as the milling medium. The required amount of powder mixture for 15:1:1 ball to powder to ethanol mass ratio (BPMR) was taken from the homogeneous mixture and placed in the bowl for ball milling. The raw materials were milled in air at room temperature for 20 h. The rotation speed of the disk was 210 rpm and that of the vials was 525 rpm. Calcination of all the powders was carried out at 650 °C for 2 h to obtain the single phase $ZnNb_2O_6$. The calcined powders were mixed with 3 wt% PVA as a binder and compacted into cylindrical pellets of 10 mm diameter and ~6 mm thickness by using a uniaxial press at a pressure of 150 MPa. The pellets were then sintered at 975–1100 °C for 1–5 h in ambient atmosphere. The density of sintered pellets was measured using the Archimedes method. The sintered pellets were analyzed by powder X-ray diffraction (XRD) to check the reflections of the phase, using Cu K_α radiation (XRD, Bruker AXS D8 Discover, Germany). Microstructures were analyzed by scanning electron microscopy (SEM, Hitachi S-4800, Japan). The ε_r and $Q \times f$ at microwave frequencies were calculated based on the size of the samples and the frequency of the TE_{011} mode using the Hakki–Coleman dielectric resonator method [27,28]. An Agilent 8720 ES network analyzer was used to measure the frequencies τ_f at microwave frequencies was measured by noting the temperature variation of the resonant frequency of $TE_{01\delta}$ mode in the reflection configuration between 25 and 85 °C, and was calculated using the following equation:

$$\tau_f\ (\mathrm{ppm}/^\circ C) = \frac{f_{80} - f_{25}}{f_{25} \times 60} \times 10^6,$$

where f_{85} and f_{25} are the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

3. Results and discussion

The characteristics of the ultra-fine $ZnNb_2O_6$ nanopowders synthesized by high energy ball-milling have been reported in detail elsewhere [26]. Morphologies (SEM and TEM micrographs) of the synthesized powder at 650 °C for 2 h are shown in Fig. 1(a) and (b). The diffraction pattern of the as-received powder is embedded in TEM micrograph. It is estimated that the particle size is within the range 30–200 nm, averaging at about 100 nm. It can be seen that small particles < 20 nm are also present in Fig. 1(b). Using the selected area diffraction (SAD) aperture of 100 nm diameter, one can deduce a nanoscale range for the crystallite size of the powder due to the existence of multispot rings in the TEM pattern.

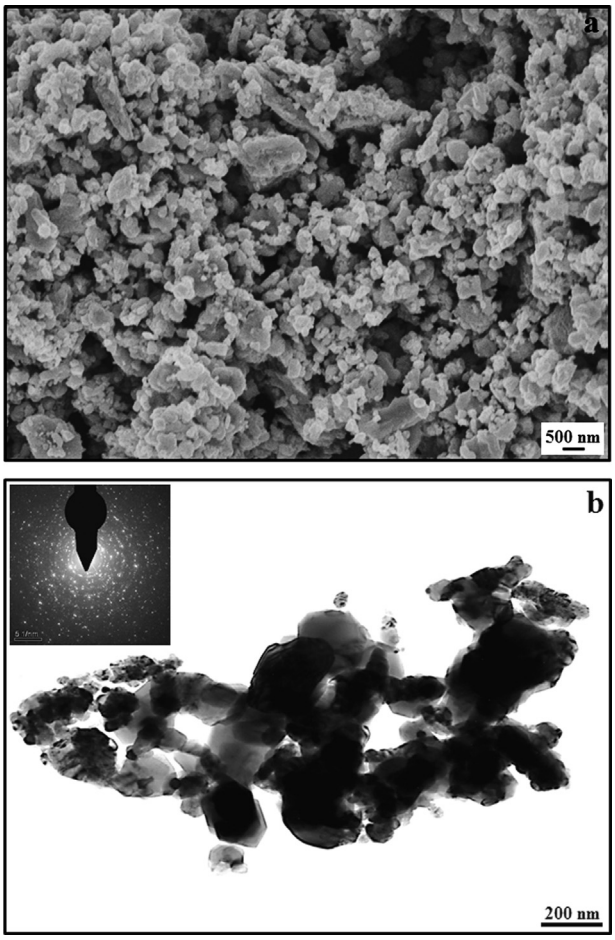

Fig. 1. SEM (a) and TEM (b) micrographs of the synthesized powder at 650 °C for 2 h.

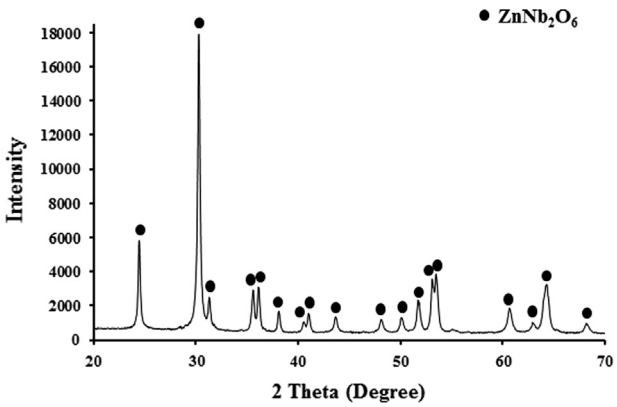

Fig. 2. X-ray diffraction pattern of the synthesized powder at 650 °C for 2 h.

The XRD of the powder is shown in Fig. 2 and all peaks are matched with JCPD file no. 01-076-1827.

The XRD patterns of $ZnNb_2O_6$ ceramics sintered at 975–1100 °C for different soaking times are shown in Fig. 3