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Production of nanoscale $Ba(Zn_{1/3}Nb_{2/3})O_3$ microwave dielectric ceramics by polymerised complex method

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ABSTRACT

$Ba(Zn_{1/3}Nb_{2/3})O_3$ nanoparticles have been synthesized by a polymerised complex method by using precursor materials of barium nitrate, zinc acetate, niobium oxide, hydrofluoric acid and citric acid. Thermal decomposition characteristics and crystallization behavior of the powders were investigated by the thermogravimetric and differential thermal analysis, X-ray diffractometer and Fourier transform infrared spectroscopy. $Ba(Zn_{1/3}Nb_{2/3})O_3$ phase started to form at low temperature of 400 °C and, single phase $Ba(Zn_{1/3}Nb_{2/3})O_3$ perovskite structure was obtained at 1000 °C. Microstructural investigation revealed that the major particle size of $Ba(Zn_{1/3}Nb_{2/3})O_3$ nanoparticles were in the range of 80–110 nm with spherical morphology and homogeneous size distribution. But the powders also contained some agglomeration.

1. Introduction

Although there has been considerable amount of work in the area of dielectric oxides in the past 50 years, dielectric materials continue to remain a significant area of scientific research due to their wide range of applications such as resonators, filters and tuners. Most of these dielectric materials are formed by the connection of metal-oxygen octahedras to each other to form principally three-dimensional structures. Among these dielectric oxides, $BaTiO_3$ which has a simple perovskite type structure and has wide ranging applications in electronic industry is probably the best dielectric ceramic of the century [1].

In addition to simple perovskites, complex perovskite structures such as niobium and tantalum based $AB_{1/3}B'_{2/3}O_3$ oxides (A = Ba; B = Mg, Zn, Ni; B′ = Ta, Nb) are novel microwave dielectric materials that have been used in dielectric applications such as mobile communication, global positioning system and base station filtering technology [2]. Microwave dielectric materials are required to have high dielectric constant ($\varepsilon_r > 30$), low dielectric loss, good temperature stability of frequency in a wide spectral range and good mechanical and thermal stability as they are investigated in terms of electrical properties [3]. Beside satellite systems and mobile communication, microwave dielectric materials are used in multi-layer ceramic capacitors and various kinds of detectors such as thermal, pressure, vibration and radiation.

$Ba(B'_{1/3}B''_{2/3})O_3$ microwave dielectric ceramics (B′ = Mg, Zn, Ni; B″ = Ta, Nb) which have complex perovskite structure have gained a giant importance for the last 20 years after the discovery of $Ba(Zn_{1/3}Ta_{2/3})O_3$ ceramics. The group of ceramics such as $Ba(Zn_{1/3}Ta_{2/3})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$ and $Ba(Mn_{1/3}Ta_{2/3})O_3$ have excellent microwave dielectric properties [4,5]. Improvement of cheaper materials that have similar properties with $Ba(Zn_{1/3}Ta_{2/3})O_3$ microwave dielectric ceramics has become important since Ta_2O_5 is an expensive oxide. In recent years, one of the materials that has been improved as a result of the studies is the $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) ceramic [6]. As compared with Ta_2O_5, Nb_2O_5 has the same crystal structure, similar ionic radius (0.64 Å) and electronic structure. The most importantly Nb_2O_5 is rather cheaper than Ta_2O_5.

$Ba(Zn_{1/3}Nb_{2/3})O_3$ oxide is a cubic perovskite ceramic and it is a member of $Pm3m$ space group. High temperature sintering makes $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic to have disordered cubic structure, on the other hand sintering below 1350 °C makes it to have ordered hexagonal structure which belongs to $P{-}3m1$ space group that introduces lower symmetry [7,8]. $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic has a high dielectric constant, low dielectric loss and high resistivity ($\varepsilon_r = 38$, Qxf = 90 THz). These electrical properties cause $Ba(Zn_{1/3}Nb_{2/3})O_3$ dielectric ceramic become a popular material in the communication industry and also increase the usage potential in applications such as capacitors and high frequency resonators. However, the temperature coefficient of resonant frequency of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic is high ($\tau_f = 30$ ppm/K) which

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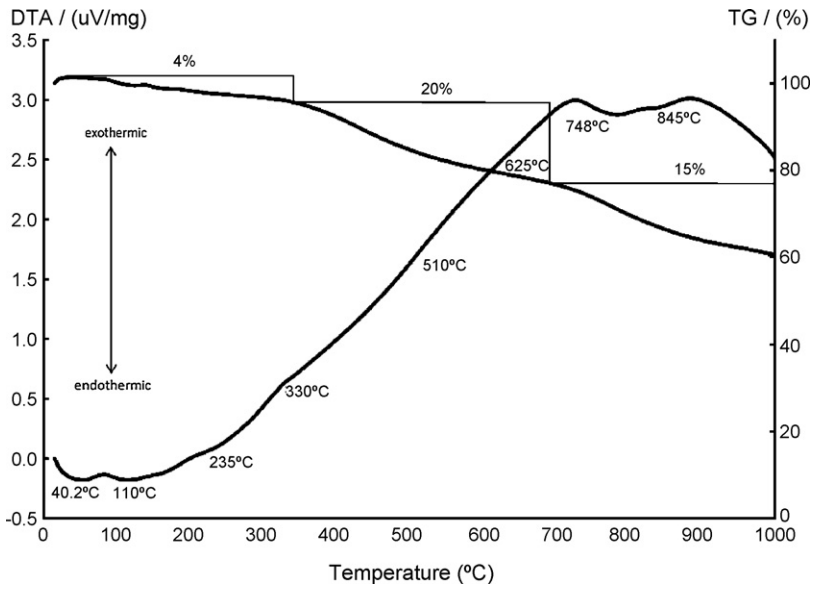

Fig. 1. TG–DTA curves of $Ba(Zn_{1/3}Nb_{2/3})O_3$ gel charred at 300 °C for 2 h.

restricts the use of these ceramics in microwave applications. Various methods have been applied to improve the properties of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics such as doping with different elements like Ti [9] or making composite of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics with other $Ba(B'_{1/3}B''_{2/3})O_3$ microwave dielectric ceramics (B′ = Mg, Zn, Ni; B″ = Ta, Nb) like $Ba(Zn_{1/3}Nb_{2/3})O_3$–$Ba(Ni_{1/3}Nb_{2/3})O_3$ [10]. $0.35(Ba(Ni_{1/3}Nb_{2/3})O_3)$–$0.65(Ba(Zn_{1/3}Nb_{2/3})O_3)$ composite microwave dielectric material which was sintered at 1450 °C for 4 h and annealed for at 1300 °C for 72 h exhibited good dielectric properties: temperature coefficient of resonant frequency (τ_f) of +0.6 ppm °C^{-1}, relative permittivity of 35 and quality factor in excess of 25,000 GHz [10]. The other drawback with $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramics is that they require fairly high sintering temperatures. In this respect, different methods such as synthesis by chemical methods or production with additives that were applied to different electronic ceramics can be applied to $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic to lower its sintering temperature and improve its microwave properties.

In this paper, $Ba(Zn_{1/3}Nb_{2/3})O_3$ nanoparticles were produced by citrate gel method which is a suitable chemical method for nanoscale powder production and never used before in the production of $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic. As compared with mixed oxide route, citrate gel method leads to formation of $Ba(Zn_{1/3}Nb_{2/3})O_3$ at lower temperatures. Single phase $Ba(Zn_{1/3}Nb_{2/3})O_3$ ceramic was characterized by various methods like TG–DTA, XRD, FT-IR, SEM and TEM.

2. Experimental details

$Ba(Zn_{1/3}Nb_{2/3})O_3$ perovskite ceramic was synthesized by citrate gel method by using barium nitrate [$Ba(NO_3)_2$] (99%, Merck), zinc acetate [$Zn(OOCCH_3)_2{\cdot}2H_2O$] (98.0–101.0%, Alfa Aesar) and niobium oxide [Nb_2O_5] (99.9%, Alfa Aesar) as starting materials. Stoichiometric amounts of niobium oxide were dissolved in minimum amount of hydrofluoric acid [HF] (38–40%, Merck) after heating in a hot water bath for 24 h to form NbF_5 solution. Niobium in NbF_5 solution was precipitated as niobium hydroxide by 2N NaOH (97%, Merck) solution. The pH was maintained around 11 to ensure completion of the reaction. $Nb(OH)_5$ powders were filtered and washed with 5% ammonia solution. Fresh niobium hydroxide precipitates were dissolved

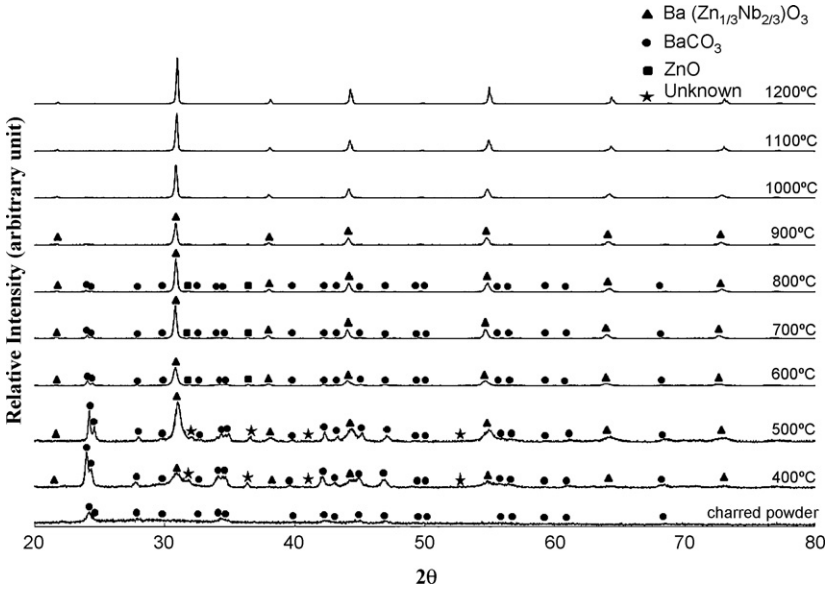

Fig. 2. X-ray diffraction patterns of $Ba(Zn_{1/3}Nb_{2/3})O_3$ powders heat treated at different temperatures for 4 h.