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Microstructure and dielectric properties control of $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ microwave ceramics

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Abstract

Microwave ceramics of $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ with 0–3 wt% Ag additions were synthesized by a citrate sol–gel method. The $BaO–B_2O_3–SiO_2$ glass was also added into the sol–gel derived BNST ceramic powders as sintering aids. The undoped, Ag- and BaBS-doped samples can be sintered at 1250 °C, 1150 °C and 1000 °C, respectively. The microstructure and dielectric properties were then controlled by doping Ag or BaBS glass. Near isoaxial grains with about 250 nm and typical columnar grains were obtained for the silver-doped and BaBS-doped samples, respectively. For the <1 wt% silver-doped samples, the dielectric constant and $Q \times f$ retained unaltered but τ_f decreased from 9 ppm/°C to 1.4 ppm/°C. With increasing silver content from 1 wt% to 3 wt%, the dielectric constant and τ_f significantly increased but $Q \times f$ decreased. For the BaBS-doped samples, both dielectric constant and $Q \times f$ decreased but τ_f increased with increasing BaBS content.

Keywords: Ceramics; Dielectrics; Microstructure; Low-temperature sintering

1. Introduction

With the recent progress of microwave integrated circuits, low dielectric loss materials with a high dielectric constant and a near-zero temperature coefficient of resonant frequency have been increasingly required for commercial microwave applications [1]. In particular, with the miniaturization and integration of electronic circuits, small-scale microwave devices are increasingly required. Therefore, the dielectric ceramics with submicron- or nano-sized grains and relatively low sintering temperature are required for the micro-chip microwave capacitors and multilayer dielectric filters. The investigation of lowering sintering temperature has been extensively carried out by many researchers. However, there are few reports, to our knowledge, concerning about the microstructure control for microwave dielectric ceramics. Therefore, controlling the microstructure, such as grain size, in order to cope with thinning the layer thickness is still a challenge.

The tungstenbronze-type like $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ solid solutions have been extensively studied because of their suitability for microwave applications [2–6]. The dielectric characteristics of these solid solutions are sensitive to both the value of x and the identity of the rare-earth ions. The most attractive microwave dielectric properties of high ε_r (80–84), high $Q \times f$ value (9000–10,000 GHz), and near-zero τ_f were obtained in Nd- or La-substituted $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.6$, 0.67 and 0.75) solid solution [7]. However, the high sintering temperature, usually above 1350 °C [6,8], limited the extension of practical applications. Some attempts had been carried out to lower the sintering temperature by adding low melting point oxides or glass compositions with low softening temperature. Unfortunately, by those ways it is difficult to lower the sintering temperature and control microstructure as well as microwave properties simultaneously. Besides, recent reports revealed that the microwave properties were also controlled by grain orientation in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics [9]. Accordingly, the microstructure of the sintered $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics might also affect their microwave dielectric properties, but few were reported.

In this paper, we prepared the modified $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ ceramics by a citrate sol–gel method. Ultrafine-grain

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BNST ceramics with fine microwave dielectric properties were obtained by sliver metal additions. As a comparison, we also modified the BNST ceramics with $BaO–B_2O_3–SiO_2$ glass (BaBS). The microstructure as well as sintering temperature of the sintered ceramics was successfully tuned by such additives with different characteristics. The effect of these two kinds of dopants on the sintering behavior, microstructure and microwave dielectric properties of the BNST ceramics was systematically discussed.

2. Experimental procedures

Samples of $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54} + y$ Ag ($y = 0$–5 wt.%) were prepared from high-purity $Ba(CH_3COOH)_2$, $Nd(CH_3COOH)_3$, $Sm(CH_3COOH)_3$, $Ti(OC_4H_9)_4$, and Ag_2O, using a citrate sol–gel method. An appropriate amounts of acetate and citric acid were dissolved into deionized water; Ag_2O was dissolved into nitric acid beforehand, and butyl titanate was dissolved in citric acid solution. These solutions were then mixed together and a small amount of aqueous ammonia was added to adjust pH value to about 6. During this process, the solution was continuously stirred using a magnetic agitator at 80 °C. The mixed solution was then heated at 110 °C and a black foam-like xerogel was obtained. The xerogels were calcined in the temperature range of 700–900 °C for 4 h. For the $BaO–B_2O_3–SiO_2$ (BaBS)-doped samples preparation, the BaBS powder was added into the calcined undoped $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ powder at this step. The calcined powders were milled by planetary milling for 5 h in alcohol medium. After drying, the powders were pressed into disk-shaped compacts using uniaxial pressure of 2.5 tonnes/cm^2. The samples were sintered at 950–1250 °C for 4 h in air.

The bulk densities of the sintered samples were measured by the Archimedes method. The theoretical densities (TD) of these samples were calculated from the theoretical densities of $Ba_4Sm_{9.33}Ti_{18}O_{54}$ (5.91 g/cm^3), Ag (10.50 g/cm^3) and BaBS (2.75 g/cm^3) according to the nominal silver content. The deviation from the "real" theoretical density of $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$, is small enough to be ignored due to their similar molecular weight and unit-cell volume. The crystalline phases were determined by using an X-ray diffractometer (D/max-2500, Rigaku, Tokuo, Japan) with Cu Kα radiation. The microstructures of sintered samples and powders were observed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The dielectric constants and unloaded Q values at microwave frequencies were characterized at room temperature by the Hakki–Coleman method and cavity method [10,11]. The temperature coefficients (τ_f) of the resonance frequencies were measured in the temperature range of 25–80 °C. The τ_f value can be calculated by the following relationship [12]:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

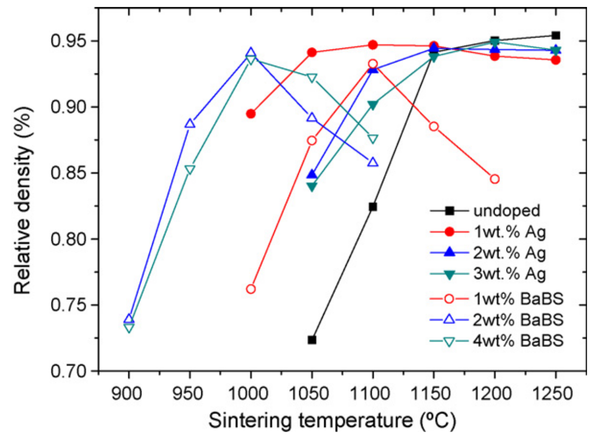

Fig. 1. Relative density variation of the undoped, Ag-doped, and BaBS-doped BNST ceramics with sintering temperatures.

3. Results and discussion

The samples of $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ (BNST) ceramics with different silver or BaBS content were sintered into dense bodies at different temperatures. The sintering temperature and relative density of each composition are listed in Table 1. The relative densities of sintered samples were plotted as a function of sintering temperatures (shown in Fig. 1). The density of undoped samples saturated at 1250 °C. This was lower than that prepared by the solid-state reaction method or the wet chemical methods, where the sintering temperatures of above 1400 °C or 1350 °C were required [8,13,14], owing to the high sinterability of the nano-powders prepared by the citrate sol–gel process. It is evident that both the silver metal and BaBS glass can improve the sinterability of the BNST ceramics. For the silver-doped samples, the sintering tempera-

Table 1
The sintering temperatures, densities and microwave properties of the modified $Ba_4(Nd_{0.7}Sm_{0.3})_{9.33}Ti_{18}O_{54}$ ceramics

Dopants	Sintering temperature (°C)	Relative density (%)	Dielectric constant	f (GHz)	$Q \times f$ (GHz)	τ_f (ppm/°C)
Undoped	1250	95.4	81.2	5.266	10,800	+9.0
0.5 wt% Ag	1150	95.5	81.1	4.606	11,000	+3.0
1 wt% Ag	1100	94.7	81.2	4.841	11,000	+1.4
2 wt% Ag	1150	94.4	84.0	4.983	6,400	+13
3 wt% Ag	1200	94.9	90.2	5.291	4,000	+19
1 wt% BaBS	1100	93.2	76.6	5.774	8,200	+13
2 wt% BaBS	1000	94.1	76.3	6.261	8,300	+18
4 wt% BaBS	1000	93.6	75.5	6.249	7,500	+25