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Microwave Dielectric Properties of Sol-Gel Derived $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$:B_2O_3 Ceramics

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Abstract. $BaTi_4O_9$ and B_2O_3-doped $Ba_2Ti_9O_{20}$ ceramics powders have been prepared by a sol-gel route. The phase evolution, grain size and dielectric properties of the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$-based ceramics powders have been investigated. These results show that the $BaTi_4O_9$ and 5 wt% B_2O_3-doped $Ba_2Ti_9O_{20}$ ceramics powders calcined at 800°C for 2 h with the grain sizes of 30–80 and 50–200 nm, respectively. Monophase sample of $BaTi_4O_9$ with orthorhombic symmetry could be obtained after the $BaTi_4O_9$ precursor was calcined at 1200°C for 2 h, whereas, monophase sample of 5 wt% B_2O_3-doped $Ba_2Ti_9O_{20}$ was obtained at 800°C for 2 h. The $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics fabricated using the sol-gel powders were found to have microwave dielectric properties with $\varepsilon_r = 36.1$, $Q = 3220$ at 5.31 GHz, and $\varepsilon_r = 34.5$, $Q = 2425$ at 5.53 GHz, respectively. The effect of sintering temperatures on the microwave dielectric properties of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics was studied.

Keywords: dielectric properties, microwave materials, ceramics, $BaTi_4O_9$, $Ba_2Ti_9O_{20}$

1. Introduction

A dielectric materials acting as a resonator was first proposed by Richtmyer in 1939 [1]. Recently, commercial wireless communication has been a rapid growing market during the past decade. This technology advancement was made possible, in part, with the recent revolution in the miniaturization of microwave circuits by using low-loss and temperature-stable dielectric resonators. Several ceramic materials have been developed for use as microwave resonators, such as $Ba(Zn,Ta)O_3$, $Ba(Mg,Ta)O_3$, $(Zr_{0.8}Sn_{0.2})TiO_4$, $BaTi_4O_9$, and $Ba_2Ti_9O_{20}$. Among the various candidates, $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ have been received much attention for their desirable microwave dielectric properties with high dielectric constant and good quality factor Q [2, 3].

The preparation of monophasic samples of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ from $BaCO_3$ and TiO_2 by conventional solid-state reaction, the stoichiometry and fabrication parameters must be precisely controlled, since there are various thermodynamically stable compounds in the vicinity of the desired composition of TiO_2-rich BaO-TiO_2 system: e.g. $Ba_6Ti_{17}O_{40}$, $BaTi_3O_7$, $BaTi_4O_9$, $BaTi_5O_{11}$, and $Ba_4Ti_{13}O_{30}$ [4, 5]. Ritter et al. reported that the monophase sample of $BaTi_4O_9$ was not completely formed into $BaTi_4O_9$ until 1300°C [6]. Xu et al. reported that the sol-gel derived single-phase $BaTi_4O_9$ could not be obtained even after the $BaTi_4O_9$ precursor was heated at 1200°C for 2 h [7]. Lu et al. also reported that the sol-gel derived sole phase $Ba_2Ti_9O_{20}$ could be obtained when the $Ba_2Ti_9O_{20}$ precursor was calcined at 1200°C for 110 h [8]. There are only a few reports on the effect of glass additions, although low-melting glass additions as liquid-phase sintering aids are cheaper and more easily lower the firing temperature. In this work, the pure phase powders and ceramics of $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ were prepared by a simple sol-gel method. The sol-gel derived single-phase $BaTi_4O_9$ could be obtained after the $BaTi_4O_9$ precursor was heated at 1200°C for 2 h. The B_2O_3 additions as liquid-phase sintering aids and more easily

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lower the firing temperature of the $Ba_2Ti_9O_{20}$ ceramics, the single-phase $Ba_2Ti_9O_{20}$ could also be obtained after the $Ba_2Ti_9O_{20}$ precursor was heated at low temperature of 800°C for 2 h. The microwave dielectric properties and the effect of sintered temperatures on the dielectric properties of the $Ba_2Ti_9O_{20}$ ceramics are reported.

2. Experimental Procedure

$BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 powders and ceramics were prepared by a sol-gel method [8]. Weighted amounts of the appropriate proportions of high purity barium acetate $Ba(CH_3COO)_2$ (purity of >99.5%), titanium *n*-butoxide $Ti(OC_4H_9)_4$ (purity of 99%) and boron oxide B_2O_3 (purity of >99%) were used as the starting materials. Acetic acid CH_3CH_2OOH (purity of >99.5%) and 2-methoxyethanol $C_3H_8O_2$ (purity of >99.5%) were selected as solvents. Barium acetate was dissolved in acetic acid and stirred for 60 min at 70°C, 5 wt% B_2O_3 was dissolved in acetic acid and stirred for 180 min at 70°C, and titanium *n*-butoxide was dissolved in 2-methoxyethanol and stirred for 30 min at 70°C, respectively. After cooling to room temperature, two or three solutions was mixed in the flask at 70°C. Then the solution is stirring for 30 min at 70°C. By controlling the hydrolysis condition of the complex solutions, the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 gels were formed. The dry gel was annealed at 700–1250°C for 2 h in atmosphere and after grinding, the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 powders were obtained. The annealed powders was dried and pressed into disks. The pellets were sintered at 1200–1300°C for 2 h and cooled in a furnace.

The crystalline phase evolution of the calcined powders has been examined by a X-ray diffraction (XRD; Philips PW3710) using Cu Kα radiation with a Ni filter. Field emission scanning electron microcope (FE-SEM, JSM-6335F, JEOL) was also used to examine the grain size and shape. Before the microwave measurements, the surfaces of the disk-shaped samples were polished with sandpaper. The dielectric properties at microwave frequency were measured by the resonant cavity method described by Hakki and Coleman [9] using the TE_{011} propagation mode coupled with an adjustable parallel plate cavity and an Agilent 8720 ES S-parameter network analyzer. The $Q \times f$ factor was used to evaluate the loss quality, where is the resonant frequency (5.52–6.29 GHz).

3. Results and Discussion

Figure 1 shows the XRD patterns of the $BaTi_4O_9$ precursor that has been calcined at different temperatures in air atmosphere (700, 750, 800, 1000, 1100 and 1200°C) for 2 h. The precursor starts to crystallize at 700–750°C, the major phase can be identified as a mixture of barium carbonate $BaCO_3$, barium titanate $BaTiO_3$ and $BaTi_4O_9$. After calcining at 800°C for 2 h (Fig. 1(c)), the main diffraction peaks of the $BaTi_4O_9$ phase are already observed along with a small amount of $BaCO_3$ and $BaTiO_3$, indicating that the crystallization of $BaTi_4O_9$ takes place readily even at a significantly lower temperature. According to the X-ray data, the peaks correspond to the formation of pure $BaTi_4O_9$ with orthorhombic symmetry at 1200°C for 2 h. Xu et al. reported that they are can not obtained the pure phase $BaTi_4O_9$, when the precursor after calcination at 1200°C [7]. They used $BaCO_3$ as the barium source and used HNO_3 and NH_4OH as solvents. It is known that to prepare metal oxide powders by sol-gel process, the best metal source is metal alkoxide, then is acetate, thirdly is nitrate, the final is carbonate. So, the barium acetate as barium source is better than that of barium carbonate.

Figure 2 shows the XRD patterns of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 precursor that has been calcined at

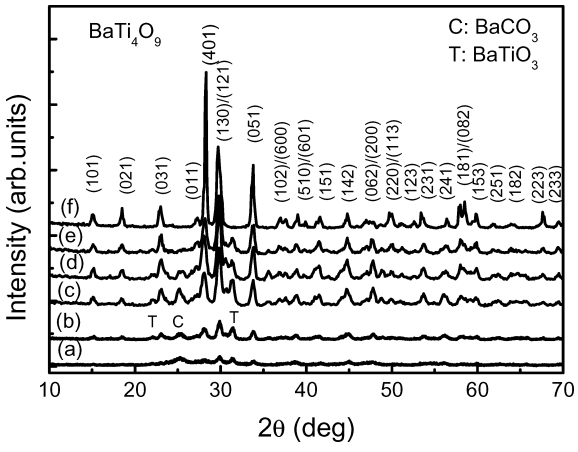

Fig. 1. X-ray diffraction patterns of the $BaTi_4O_9$ powders calcined at different temperatures for 2 h: (a) 700, (b) 750, (c) 800, (d) 1000, (e) 1100, (f) 1200°C.

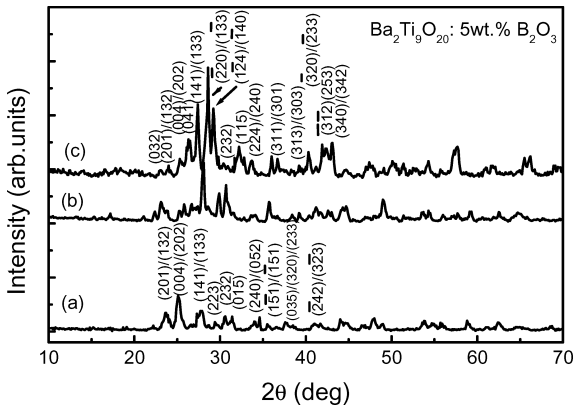

Fig. 2. X-ray diffraction patterns of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 powders calcined at different temperatures for 2 h: (a) 800, (b) 1050, and (c) 1250.

different temperatures for 2 h in air atmosphere (800, 1050, and 1250°C) for 2 h. As the calcined temperature was 800°C, the powders crystallized to triclinic phase $Ba_2Ti_9O_{20}$. The plane indexes are marked in Fig. 2. Wang et al. reported that the series of pure $Ba_2Ti_9O_{20}$ were obtained by used 5 wt% B_2O_3 [10], 2.8 wt% TiO_2 and 4 wt% ZrO_2 [11]. The pure $Ba_2Ti_9O_{20}$ phase was obtained at the low temperature of 900°C because the eutectic reaction could increase the volume of liquid phase and accelerate the migration of reactant species through the liquid phase formed between the grains in the pellet. Lee et al. reported that pure $Ba_2Ti_9O_{20}$ was obtained by use $3ZnO–B_2O_3$ [12]. B_2O_3 was dissolved in acetic acid to formed solution at first, and then added it to Ba-Ti-solution. Therefore, the uniformly Ba-Ti-B-solution can be obtained. The overall reactions were performed in solvents, and could promote the further lowering of reaction temperature to the 800°C.

Figure 3 shows the FE-SEM micrographs of the sol-gel derived $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramic powders calcined at 800°C for 2 h. The particle morphology is almost spherical, with a grain size of 30–80 nm and 50–200 nm, respectively for the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramic powders.

The dielectric constants (ε_r) and Q factors of the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 microwave ceramics were measured at room temperature by an Agilent 8720 ES S-parameter network analyzer. $BaTi_4O_9$ ceramic was sintered at 1250°C for 2 h, it has good properties (the resonant frequency f, ε_r, Q factor and $Q \times f$ factor were 5.31 GHz, 36.1, 3220, and

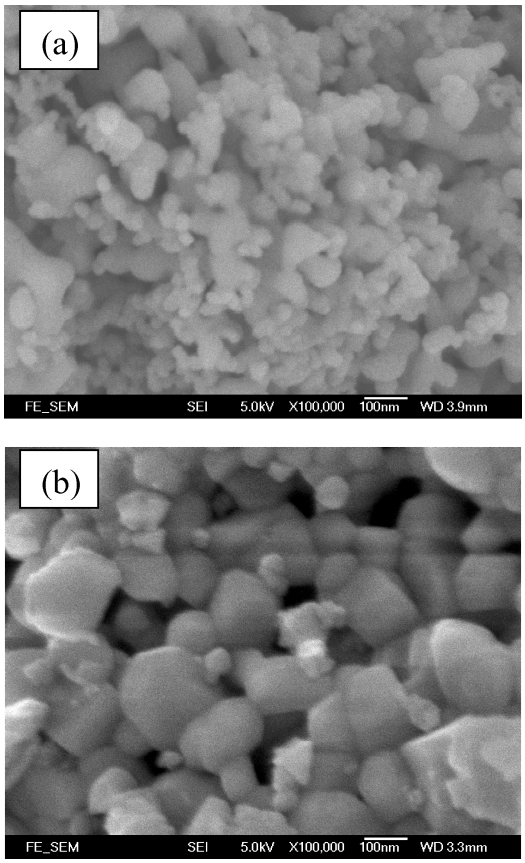

Fig. 3. FE-SEM photographs of (a) $BaTi_4O_9$ and (b) $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 powders after calcined at 800°C for 2 h. (Magnification: ×100,000).

17100 GHz, respectively). The ε_r value is comparable with that of $BaTi_4O_9$ ceramics from an oxalates route (38 ± 0.5) [13]. A ε value of 34.2 has been reported for Sn-doped $BaTi_4O_9$ ceramics prepared by a citrate route [14].

The effect of sintering temperature on the dielectric properties of $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics are listed in Table 1. From the Table 1, it is seen that the dielectric properties of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics have almost not changed with increasing sintering temperatures. The resonant frequencies related to the thickness of the samples. For the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics sintered at 1250°C for 2 h, the resonant frequency, ε_r, Q factor and $Q \times f$ factor were 5.52 GHz, 34.5, 2425, and 13400 GHz, respectively. The dielectric constant of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics is slightly lower than that of pure $Ba_2Ti_9O_{20}$ ceramics ($\varepsilon_r = 36.9$) [15]. ε_r values of 27.3 and 28.3

Table 1. Microwave dielectric properties of the $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics sintered at different temperatures for 2 h.

Sintering temperature (°C)	Resonant frequency f (GHz)	Dielectric constant ε_r	tanδ ($\times 10^{-4}$)	Q factor (GHz)	$Q \times f$ factor
1200	5.637	34.3	3.8	2464	13800
1250	5.52	34.5	4.1	2425	13400
1300	6.29	34.9	4.0	2434	15300

have been reported for $Ba_2Ti_9O_{20}$: 3 wt% B_2O_3 and $Ba_2Ti_9O_{20}$: 1 wt% ZnBO ceramics sintered at 940°C for 2 h [12, 16].

4. Conclusions

$BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 powders with 30–80 and 50–200 nm sizes have been prepared via a sol-gel route, respectively. The phase evolution, physical and dielectric properties of the $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics powders have been investigated. It is observed that the addition of the B_2O_3 glass phase in the $Ba_2Ti_9O_{20}$ ceramics can effectively lower the sintering temperature. For the sol-gel derived $BaTi_4O_9$ ceramics sintered at 1250°C for 2 h, the ε_r, Q factor and $Q \times f$ factor were 36.1, 3220 and 17,100 GHz, respectively. The sol-gel derived $Ba_2Ti_9O_{20}$: 5 wt% B_2O_3 ceramics sintered at 1300°C for 2 h exhibits optimum microwave properties of $\varepsilon_r = 34.9$ and $Q \times f = 15{,}300$ GHz.

Acknowledgments

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