JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 12, December 2007, p. 3790 - 3794

Microwave dielectric properties of $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics

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Barium tetratitanate ($BaTi_4O_9$) powder, synthesized by coprecipitation method, was used to prepare $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics with microwave dielectric properties. The structure and microwave dielectric properties were studied. $BaNd_2Ti_5O_{14}$ and $BaSm_2Ti_4O_{12}$ single-phase ceramics were obtained from $BaTi_4O_9$:Nd_2O_3=1:1 and $BaTi_4O_9$:Sm_2O_3=1:1, respectively. A multiple phases ceramic containing mainly $BaWO_4$ and small amounts of $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ was obtained from $BaTi_4O_9$:WO_3=1:1. $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3, ceramics sintered at 1375 °C for 8.5 h in air, shown good microwave dielectric properties.

(Received October 26, 2007, accepted November 27, 2007)

Keywords: Barium tetratitanate ceramics, Microstructures, Microwave dielectric properties

1. Introduction

Microwave devices are in great demand in modern microwave telecommunication systems including satellite receiver modules and cellular telephones. The dielectric material is the main component of the dielectric resonator. Dielectric resonators may be used to determine and stabilize the frequency of a microwave oscillator or as a resonant element in a microwave filter. The present tendency of the research in this field is to improve the properties of microwave components by increasing the dielectric constant to achieve miniaturization of dielectric components, reducing the dielectric loss and reducing the temperature coefficient of resonant frequency for frequency stability. In order to achieve this aim there are two ways: improving the properties of the existing materials by carefully controlling the processing techniques and, doping the existing materials.

$BaTi_4O_9$ is a dielectric material used in the microwave domain [1]. $BaTi_4O_9$ was first reported by Rase and Roy [2] in their study of the BaO-TiO_2 system. $BaTi_4O_9$ was investigated as microwave material by O'Bryan *et al.* [3-5]. The dielectric properties of $BaTi_4O_9$ with several different additives have also been investigated in the microwave region [6-9].

The addition of WO_3 to the system BaO-TiO_2 results in multiple phases including $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $BaWO_4$, and TiO_2 [7]. The BaO-$4TiO_2$-$0.1WO_3$ ceramic was found to possess excellent microwave properties as dielectric constant K = 35. Other important microwave ceramic material is based on the BaO-Nd_2O_3-TiO_2 system. Kolar *et al.* [10] and Negas *et al.* [11] determinate phase diagram and investigated the dielectric properties at 1 MHz in this system. Interesting compounds are located in the area between $BaO{\cdot}Nd_2O_3{\cdot}3TiO_2$ and $BaO{\cdot}Nd_2O_3{\cdot}5TiO_2$ with a permittivity of 70-90 and tanδ lower than $5{\cdot}10^{-4}$. A high-permittivity ceramic used extensively in telecommunications equipment is based on the $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ system [12]. Such ceramics are typically produced commercially with additions of PbO to reduce the temperature coefficient of resonant frequency to around zero ppm/k. These materials frequently contain parasitic secondary phases, the most common of which is $Nd_4Ti_9O_{24}$. When doped with Ca, a perovskite $NdTiO_3$ phase is observed, stabilized by Ca. Attractive microwave dielectric properties of high dielectric constant and good frequency stability were obtained in a Sm- or La-substituted solid solution [13]. Studies have been performed to modify the microwave dielectric properties of $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln=La, Nd, and Sm) materials by partial substitution for A- and B-site ions (such as Ca^{2+}, Sr^{2+}, Pb^{2+}, Bi^{2+} substitution for Ba^{2+}, rare-earth substitution for La^{3+}, and Zr^{4+}, Sn^{4+}, and Al^{3+} substitution for Ti^{4+}) [14-27].

The addition of Sm_2O_3 to the system BaO-TiO_2 results in increasing of frequency stability. The compositions based on the system lie on the line connecting two ternary phases of $BaO{\cdot}Sm_2O_3{\cdot}3TiO_2$ and $BaO{\cdot}Sm_2O_3{\cdot}5TiO_2$ shown small temperature coefficient of resonant frequency [28]. In these studies, the microwave ceramic materials were prepared by solid-state reaction starting from carbonates and oxides or by wet chemical methods starting from acetates and alcoxides.

In the present work, a controlled processing technique to prepare microwave materials with compositions based on the BaO-TiO_2-Nd_2O_3, BaO-TiO_2-Sm_2O_3 and BaO-TiO_2-WO_3 systems, starting from $BaTi_4O_9$ and dopant oxides, was used.

2. Experimental procedure

$BaTi_4O_9$, Nd_2O_3, Sm_2O_3 and WO_3 were chosen as starting materials to prepare dielectric ceramics for

microwave field, based on $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 systems. $BaTi_4O_9$ powders with orthorhombic symmetry were prepared by the oxalate coprecipitation method, described in our previous paper [29]. The powders mixture of $BaTi_4O_9$ and Nd_2O_3, $BaTi_4O_9$ and Sm_2O_3 and, $BaTi_4O_9$ and WO_3 were pressed into disks at a pressure of 200 MPa and sintered at 1375 °C for 8.5 h in air. The sintered ceramics were characterized by scanning electron microscopy (SEM) using a Hitachi S-2600N Scanning Electron Microscope, and by X-ray diffraction (XRD) using a Shimadzu X-Ray Diffractometer XRD-6000. CuKα1 radiation (wavelength 1.5406), LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at 25 °C with a step-scan interval of 0.020° and a step time of 10 s. The dielectric characteristics of the ceramics were measured at microwave frequency. 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 [30] using the TE011 propagation mode coupling with an adjustable parallel plate cavity and a scalar network analyzer (Model 9855 B, Hewlett-Packard, Palo Alto, CA).

3. Results and discussion

3.1. Microstructure and densification

Figs. 1(a)-(d) show the SEM microstructures of $BaTi_4O_9$, $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics sintered at 1375 °C for 8.5 h.

The grain size of $BaTi_4O_9$ ceramics sintered at 1375 °C for 8.5 h (Fig. 1(a)) was 4-6 μm. Some pores were residual at grain boundaries or triple points suggesting an incomplete densification of sintered pellets. The surface SEM micrograph of $BaTi_4O_9$-Nd_2O_3 samples sintered at 1375 °C for 8.5 h is shown in Fig. 1(b). $BaTi_4O_9$-Nd_2O_3 ceramics show typical columnar grain morphology. The "column" was quite short compared with that of $BaTi_4O_9$. The grain size of the isotropic ones was about 2-3 μm. Adding Nd_2O_3 to $BaTi_4O_9$ lead to increase of the $BaTi_4O_9$ ceramics porosity. Fig. 1(c) illustrates the sintered surface of $BaTi_4O_9$-Sm_2O_3 ceramics at 1375 °C for 8.5 h, showing that the main crystals were bar-shaped with various lengths and thickness. The size of the crystal bars was about 3-5 μm. A well-compacted ceramic was obtained by doping of $BaTi_4O_9$ with Sm_2O_3. The surface SEM micrograph of $BaTi_4O_9$-WO_3 ceramics fired at 1375 °C for 8.5 h in air is shown in Fig. 1(d). Much different grain morphologies with small bars and block-shaped crystals, was obtained. The domain of grain size was 2-8 μm. However, the densification degree of $BaTi_4O_9$-WO_3 ceramics was good.

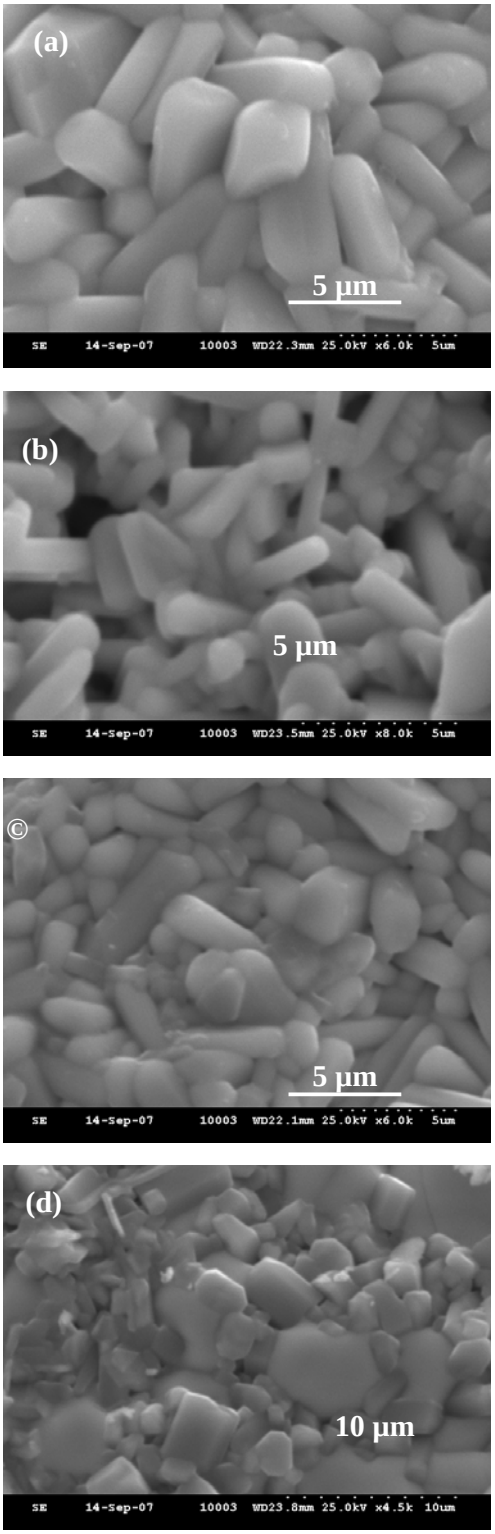

Fig. 1. Scanning electron micrographs of (a) undoped $BaTi_4O_9$, (b) $BaTi_4O_9$-Nd_2O_3, (c) $BaTi_4O_9$-Sm_2O_3 and (d) $BaTi_4O_9$-WO_3 ceramics fired at 1375 °C for 8.5 h in air

The theoretical density (calculated) of $BaTi_4O_9$ is 4.53g/cm^3. The theoretical densities for the $BaTi_4O_9$-

Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics were calculated using Eq. (l),

$$D = (W_1+W_2)/ (W_1/D_1+W_2/D_2) \quad (1)$$

where, W_1, and W_2, are the weight percentages of the $BaTi_4O_9$ dielectric and oxides (Nd_2O_3/Sm_2O_3/WO_3) in the mixtures, respectively; D_1, and D_2, are the densities of the $BaTi_4O_9$ dielectric and Nd_2O_3/Sm_2O_3/WO_3, respectively [1]. The theoretical densities calculated with Eq. (1) were: $D_{BaTi4O9\text{-}Nd2O3}$=5.39g/cm^3, $D_{BaTi4O9\text{-}Sm2O3}$=5.35 g/cm^3, $D_{BaTi4O9\text{-}WO3}$=5.16 g/cm^3. The sample densities were measured using the Archimedes method. The relative density of $BaTi_4O_9$ ceramic prepared by the coprecipitation route was 92.41%. Only 90.87% theoretical density was obtained for $BaTi_4O_9$-Nd_2O_3 ceramic sintered at 1375 °C for 8.5 h in air. Better relative densities values were obtained for $BaTi_4O_9$-Sm_2O_3 (94.20%) and $BaTi_4O_9$-WO_3 (95.34%) ceramics sintered in the same conditions. The results are in good agreement with the SEM observations (Fig. 1).

3.2. XRD analyses

The X-ray diffraction patterns (CuK_α radiation) for $BaTi_4O_9$, $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics sintered at 1375 °C for 8.5 h are shown in Fig.2-Fig. 5.

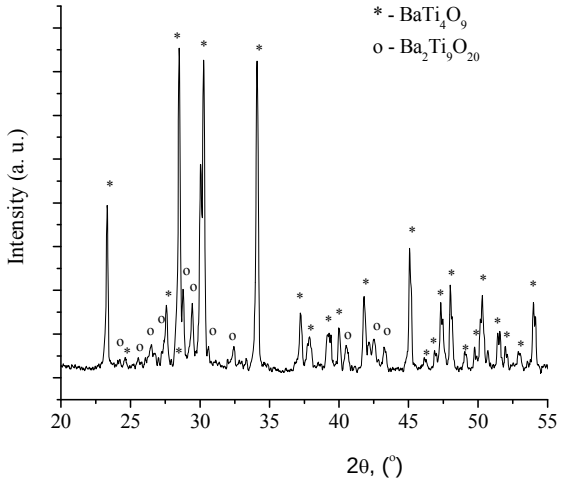

Fig. 2. XRD of undoped $BaTi_4O_9$ ceramic fired at 1375 °C for 8.5 h in air.

X-ray diffraction analysis indicated $BaTi_4O_9$ as the main crystal phase and $Ba_2Ti_9O_{20}$ as the minor phase in the undoped $BaTi_4O_9$ ceramic pellets, sintered at 1375 °C (Fig.2). The reflections were indexed with orthorhombic symmetry of $BaTi_4O_9$ [31] and triclinic $Ba_2Ti_9O_{20}$ phase [32]. A small amount of $Ba_2Ti_9O_{20}$ in $BaTi_4O_9$ ceramic is accepted because $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ are the most common high-Q dielectric materials used in the microwave range. Figure 3 shows the X-ray diffraction pattern of $BaTi_4O_9$-Nd_2O_3 ceramic fired at 1375 °C.

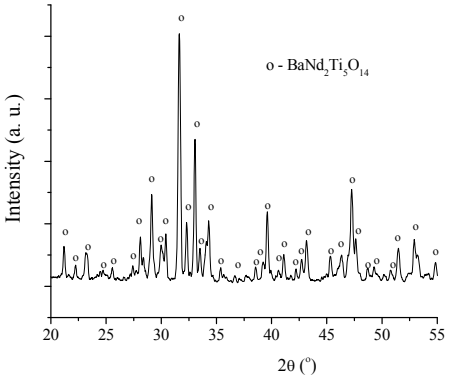

Fig. 3. XRD of $BaTi_4O_9$-Nd_2O_3 ceramic fired at 1375 °C for 8.5 h in air.

Well-crystallized and pure orthorhombic $BaNd_2Ti_5O_{14}$ [33] was formed at 1375 °C (Fig.3). Figure 4 shows the X-ray diffraction pattern of $BaTi_4O_9$-Sm_2O_3 ceramic sintered at 1375 °C.

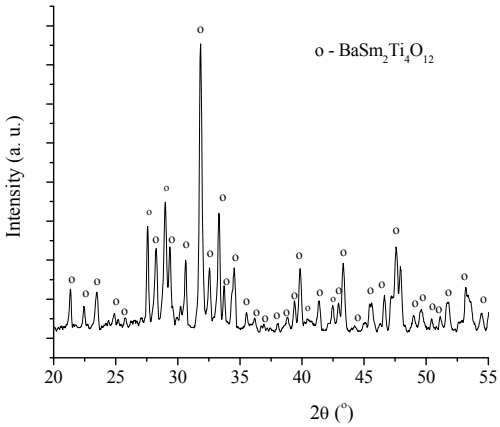

Fig. 4. XRD of $BaTi_4O_9$-Sm_2O_3 ceramic fired at 1375 °C for 8.5 h in air.

The diffraction profiles are consistent with pure and orthorhombic $BaSm_2Ti_4O_{12}$ phase [34]. The results of X-ray diffraction of $BaTi_4O_9$-WO_3 sintered pellets are shown in Fig. 5.

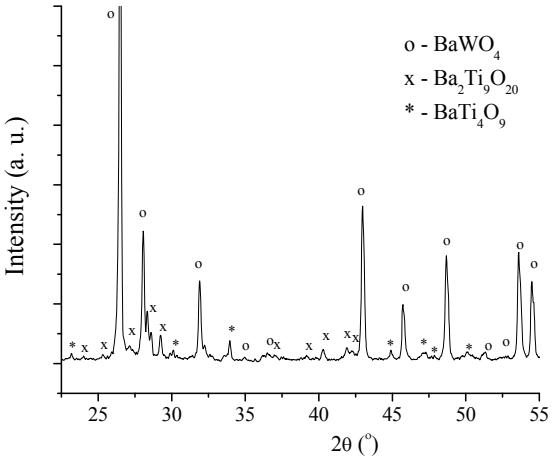

Fig. 5. XRD of $BaTi_4O_9$-WO_3 ceramic fired at 1375 °C for 8.5 h in air.

According to the XRD results, $BaTi_4O_9$-WO_3 ceramic consist of $BaWO_4$, $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$ phases. The reflections were indexed with tetragonal symmetry of $BaWO_4$ [35], triclinic $Ba_2Ti_9O_{20}$ [32] and orthorhombic $BaTi_4O_9$ [31] phases. The crystal phases after 8.5 h of sintering at 1375 °C were mainly $BaWO_4$, as well as small amounts of $Ba_2Ti_9O_{20}$ and $BaTi_4O_9$.

3.3. Microwave dielectric properties

The best dielectric properties obtained in the present study for $BaTi_4O_9$, $BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and $BaTi_4O_9$-WO_3 ceramics are presented in Table I.

Table I. The dielectric properties of Nd_2O_3-, Sm_2O_3- and WO_3-$BaTi_4O_9$ ceramics sintered for 8.5 h, at 1375 °C.

Sample	f_r, (GHz)	Δf, (GHz), $x10^{-3}$	ε_r	$tg\delta$, $x10^3$	Q
$BaTi_4O_9$	7.16	7.38	36.7	1.0	1000
$BaTi_4O_9$-Nd_2O_3	6.67	12.63	49.3	1.9	526
$BaTi_4O_9$-Sm_2O_3	4.51	6.07	61.2	1.3	769
$BaTi_4O_9$-WO_3	5.47	13.67	25.1	2.5	400

The microwave dielectric properties are influenced by the compositional uniformity, structural homogeneity and the density of the sintered samples. Considering the dielectric properties of each phase $BaTi_4O_9$, $Ba_2Ti_9O_{20}$, $BaNd_2Ti_5O_{14}$, $BaSm_2Ti_4O_{12}$ and $BaWO_4$, the dielectric properties obtained in this work are in good agreement with literature data.

4. Conclusions

$BaTi_4O_9$-Nd_2O_3, $BaTi_4O_9$-Sm_2O_3 and, $BaTi_4O_9$-WO_3 microwave ceramics were prepared from $BaTi_4O_9$ and corresponding oxides. The influence of Nd_2O_3, Sm_2O_3, and WO_3 on the sinterability, structure and dielectric properties of the $BaTi_4O_9$ ceramics was investigated. The following conclusions could be obtained.

Adding neodymium, samarium and tungsten oxides to $BaTi_4O_9$ produce morphological and dielectric changes to $BaTi_4O_9$ ceramic, as a function of the nature of oxides. Nd_2O_3 added to $BaTi_4O_9$ decreases the grains size, increases the porosity and decrease the density of $BaTi_4O_9$ ceramics due to the new phase ($BaNd_2Ti_5O_{14}$) that appear. Sm_2O_3 reacts with $BaTi_4O_9$ at high temperature resulting $BaSm_2Ti_4O_{12}$ compound with good sinterability. The ceramic obtained from a mixture $BaTi_4O_9$:WO_3 with molar ratio=1:1 was multiple-phases with inhomogeneous grains size, were grains of 2μm coexist with abnormal grains grown of 8 μm.

All ceramics obtained from $BaTi_4O_9$ and neodymium oxide, samarium oxide and tungsten oxide shown good dielectric properties for microwave applications.

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