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Preparation and microwave dielectric properties of $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics via a citrate sol-gel process

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Recently, microwave dielectric ceramics have been widely investigated due to the rapid progress in wireless communication. The dielectric properties required for the dielectric ceramics used in resonators are high dielectric constant, high-Qf value, and good temperature stability [1]. Ceramics based on $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ tungsten-bronze type solid solution are widely used in microwave resonators and filters due to their high dielectric constant and low loss [2].

The conventional solid-state reaction method is commonly used to prepare microwave dielectric ceramics, but the inevitable inhomogeneity derived from mechanically mixing can destroy the compositional and microstructural homogeneity of sintered products, and lower the dielectric properties of the final products. Wet chemical methods can overcome such shortcomings. Some wet chemical methods, such as coprecipition [3] and sol-gel [4, 5] have been utilized to synthesize pure $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics. However, only a few references [4] have reported the microwave dielectric properties.

In this letter, the preparation of $Ba_4(Sm_{1-x}Nd_x)_{9.3}$-$Ti_{18}O_{54}$ ceramics from a modified Pechini method, in which citric acid was used as a chelating agent is reported. The phase development, microstructure and microwave dielectric properties were investigated.

$Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramic powders with $x = 0$, 0.1, 0.2, and 0.3, denoted as BSNT-1, BSNT-2, BSNT-3, and BSNT-4 respectively, were synthesized by the citrate sol-gel route using high pure $Ba(NO_3)_3$, Sm_2O_3, Nd_2O_3, nitric acid, butyl titanate ($Ti(OC_4H_9)_4$), and $NH_3{\cdot}H_2O$ as raw materials. Appropriate amounts of Nd_2O_3 and Sm_2O_3 were first dissolved in diluted nitrite acid. $Ba(NO_3)_3$ and butyl titanate, which will form 40 g of ceramic powder, were dissolved in 500 ml of deionized water. After the two solutions were mixed together, a small amount of ammonia was added to adjust the PH value to about 6. During this process, the solution was continuously stirred using a magnetic agitator. The mixed solution was then poured into a dish and heated at 120 °C stirring constantly to transform into a xerogel. The xerogels were heated in temperature range 600 to 1100 °C in order to acquire pure tungsten-bronze type compounds.

The phase formation process was studied by X-ray diffraction analysis using a Rigaku D/MAX IIIB X-ray diffractometer (XRD) with Cu K_α radiation. Fig. 1 shows the XRD patterns of BSNT-1 powders calcined at different temperatures. For comparison the XRD pattern of the sample sintered at 1350 °C is also included in Fig. 1. It can be seen that the as-obtained powders are amorphous in nature. The crystalline phases appear only above 900 °C. At 1100 °C, the pure tungsten-bronze phase was formed. This temperature is lower than that for the solid-state method, in which the pure tungsten-bronze phases are usually formed above 1200 °C. Other powders with different compositions are similar to sample BSNT-1. These results indicate that the highly reactive microwave ceramic powders can be synthesized by the present citrate sol-gel process.

In order to evaluate the sintering behavior of the synthesized powders, thermo-mechanical analysis (TMA) was used to characterize the sinter shrinkage. Fig. 2 shows the shrinkage and shrinkage rate as a function of temperature for the pressed BSNT-1 sample. It demonstrates that the onset of shrinkage takes place at ~1100 °C. The maximum shrinkage rate occurs at ~1300 °C. This suggests that the synthesized powder can be sintered at ~1300 °C for several hours, a lower temperature than that for powders prepared by the solid-state method.

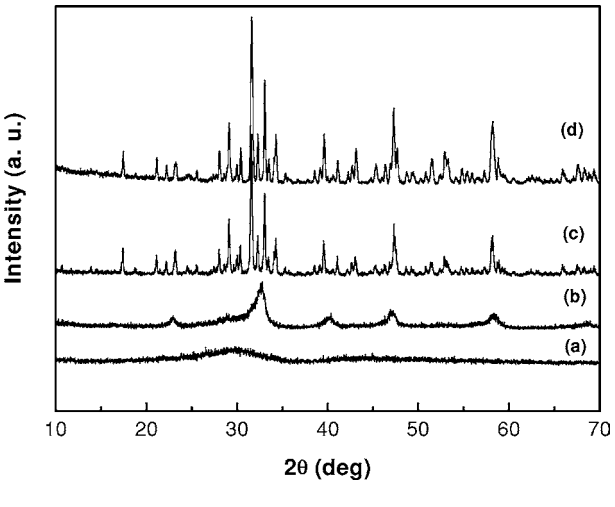

Figure 1 XRD patterns of BSNT-1 powders calcined at (a) 600 °C, (b) 900 °C, (c) 1100 °C, and (d) as-sintered ceramic at 1350 °C.

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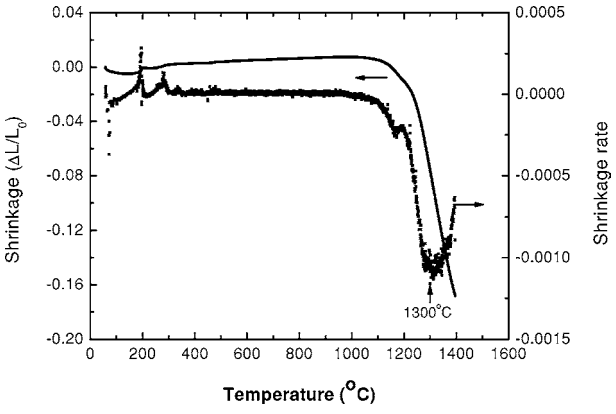

Figure 2 Shrinkage and shrinkage rate as a function of temperature for synthesized BSNT-1 powder.

The synthesized powder was mixed with 5 wt% poly(vinyl alcohol) as a binder, granulated, and uniaxially pressed at a pressure of 150 MPa to form green specimens. The specimens were sintered at 1350 °C for 5 h. The bulk densities of the sintered pellets were measured by the Archimedes method and the data are summarized in Table I.

Microstructural characterization was conducted by scanning electron microscopy (SEM). Fig. 3 shows the SEM photomicrographs of sintered samples with different compositions. It can be seen that dense microstructures with relatively uniform grains were formed after sintering at 1350 °C. Neodymium substitution for samarium in $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics has little influence on the grain shape and size. With increasing neodymium content, the grain size increases slightly and the grain shape becomes more rodlike.

TABLE I Microwave dielectric properties of $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics

x	Density (g-cm^{-3})	f_0 (GHz)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0.0	5.785	5.06	80.3	9056	−10.5
0.1	5.733	5.09	80.1	9100	−5.2
0.2	5.749	5.18	80.5	9220	−1.4
0.3	5.730	5.10	80.9	9531	4.6

The dielectric constant and the quality factor values at microwave frequencies were measured using the Hakki-Coleman dielectric resonator method as modified and improved by Courtney [6, 7]. A HP8720ES network analyzer was employed in the measurement. The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range +10 to +100 °C. The τ_f value can be calculated using the following relationship:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

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

The measured dielectric properties are summarized in Table I, and the variations of $Q \times f$ and τ_f values as a

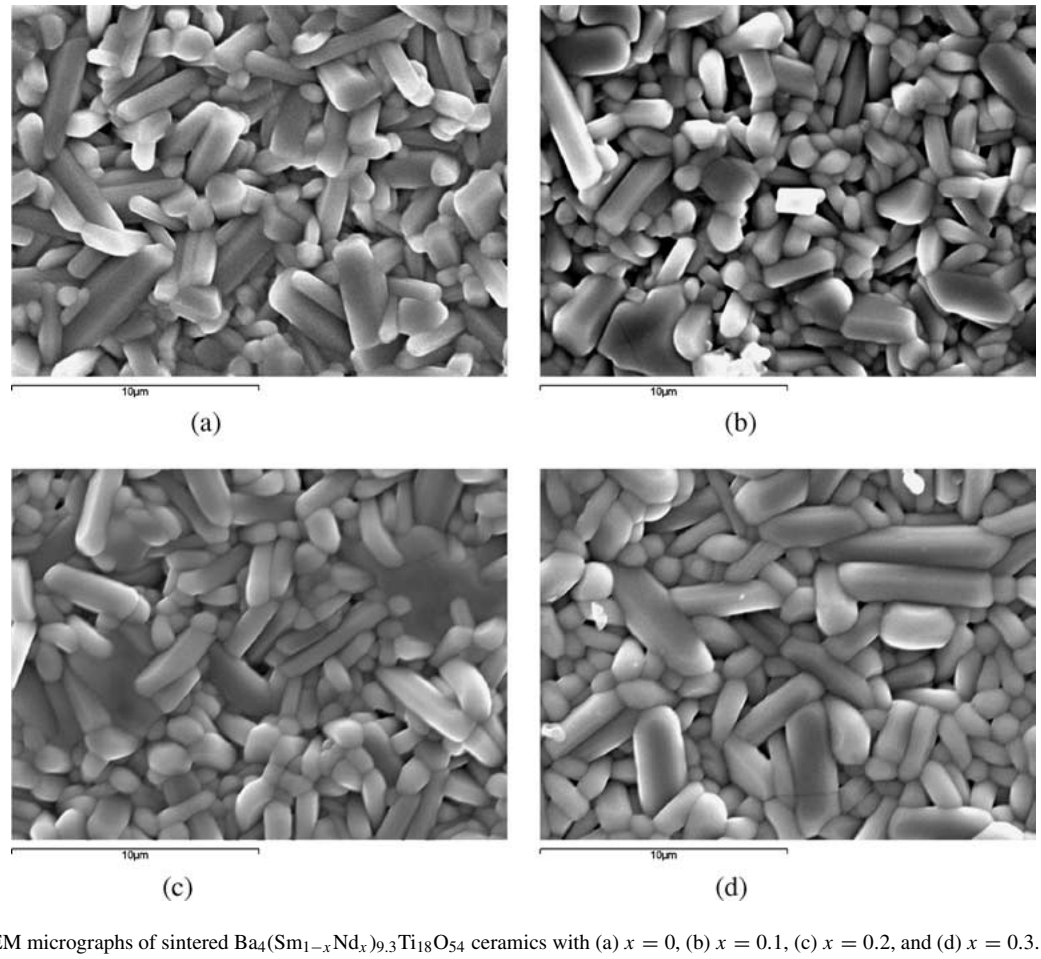

Figure 3 SEM micrographs of sintered $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics with (a) $x = 0$, (b) $x = 0.1$, (c) $x = 0.2$, and (d) $x = 0.3$.

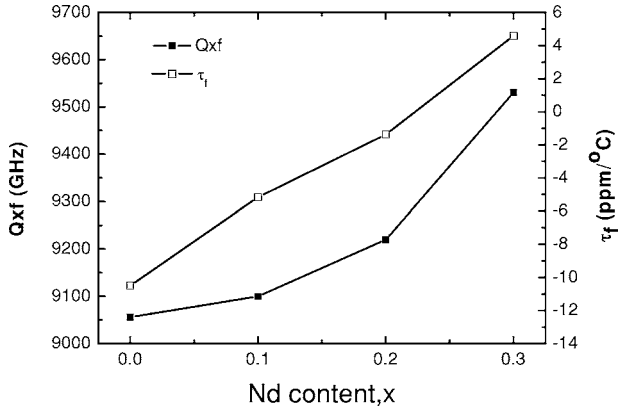

Figure 4 Dielectric properties of $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics as a function of Nd content.

function of Nd content (x) are shown in Fig. 4. It is clear from Table I that neodymium substitution for samarium in $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ ceramics in the present compositional range has no significant influence on the dielectric constant. The $Q \times f$ and τ_f values, however, depend on the Nd content, as shown in Fig. 4. With increasing Nd content from 0 to 0.3, the $Q \times f$ value increases rapidly. The τ_f value shifts from negative to positive as the x value increases from 0 to 0.3. An τ_f value of -1.4 ppm/°C was obtained at $x = 0.2$. The reasons for the variations of dielectric properties with Nd content may be from the increased grain sizes and the smaller ion diameter of Nd compared with Sm [8, 9].

Summarizing the present experiment results, it can be concluded that the citrate sol-gel process is an effective route to prepare tungsten-bronze type microwave ceramics with high quality factors. The synthesized precursor powders can transform into pure tungsten-bronze phases at low temperatures relative to those for powders produced by conventional solid-state methods. The prepared ceramics with compositions of $Ba_4(Sm_{1-x}Nd_x)_{9.3}Ti_{18}O_{54}$ have excellent dielectric properties. A ceramic with a dielectric constant of 80.5, $Q \times f$ value of 9220 GHz and τ_f value of -1.4 ppm/°C was obtained at $x = 0.2$.

Acknowledgments

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