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Sol–gel preparation of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ microwave dielectric ceramics

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Abstract

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powders were prepared by a sol–gel method using ethylenediaminetetraacetic acid as a complexing agent. A molecular-level, homogeneously mixed gel was obtained, and transferred into resin intermediate through charring. Well-crystallized $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ powders were prepared by calcination of the resin intermediate. DTA, TG, XRD and SEM were used to characterize the precursors and powders. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics were sintered at different temperatures and their microwave dielectric properties were evaluated. The effect of ball-milling on the microwave dielectric properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics was examined. By sintering ball-milled powder prepared by the sol–gel method, excellent microwave dielectric characteristics for $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics were obtained: $\varepsilon = 80.8$, $Q_f = 11{,}330$ GHz.

Keywords: Functional ceramics; Chemical synthesis; Powder; Microwave dielectric property

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1. Introduction

Microwave dielectric ceramics are of great interest because of their important applications as resonators, filters and oscillators in microwave communication. Three important dielectric parameters are required for these ceramics: (1) a high dielectric constant ε, (2) a high quality factor Q, and (3) a near-zero temperature coefficient of resonant frequency, τ_f. High ε reduces circuit/device size, reasonable Q allows distribution of signal with minimum loss, and low temperature coefficients avoid drift in frequency due to temperature variations. Neodymium and samarium analogues of the $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ solid solutions are of special interest because of their potential applications such as dielectric resonators and filters due to their high ε in the 80–90 range, modest Q (1.5–4 K, ~3 GHz) and low τ_f [1–6]. It is reported that the solid solution with x closed to 2/3 has the best microwave dielectric properties [1,3,4].

Usually $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics are prepared by the conventional solid-state reaction of mechanically mixed powders. The inevitable inhomogeneity affects microstructural homogeneity of sintered products. The wet chemical methods [7,8] have also been developed for the synthesis of pure, single-phase mixed oxide powders. Takahashi and Ikegami [7] used an improved coprecipitation method to prepare $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.5$) powders and ceramics. Hoffmann and Wagner [8] prepared $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.5, 0.7$) powders and ceramics by sol–gel method (propionate-route) and excellent microwave dielectric properties were obtained.

A sol–gel technique based on the formation of ethylenediaminetetraacetic acid (EDTA) complexes has been used with success in the preparation of high temperature superconductors [9], $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ [10], $BaTi_2O_5$ [11] and $LaAlO_3$ [12]. The main advantage of the method stems from the large stability constant of most EDTA complexes and the large number of elements with which EDTA forms complexes. In this paper, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) is prepared via the sol–gel route and the microwave dielectric properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics are evaluated.

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2. Experimental

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramic powders were synthesized via the EDTA gel route. Butyl titanate ($Ti(OC_4H_9)_4$, purity of >98%, Shanghai Chemical Regent No. 3 Factory), $BaCO_3$ powder (purity of >99.5%, Shanghai Chemical Reagent No. 1 Factory), Sm_2O_3 (purity of >99.5%, Shanghai Yuelong Chemical Regent Corporation Limited), EDTA (purity of >99.5%, Shantou Chemical Regent Factory) and 65–68% nitric acid (guaranteed reagent, Shanghai Chemical Reagent No. 3 Factory) were employed as the starting ingredients.

EDTA was dissolved in ammonium hydroxide solution, to which butyl titanate was added gradually with continuous stirring. The solution was heated at 80 °C on a hot plate and nitric acid was added to the stirred solution to adjust the pH to 4. When the opaque, white solution became a clear, light yellow color, then $Sm(NO_3)_3$ solution (Sm_2O_3 powder dissolved into nitric acid) and $BaCO_3$ powder were added slowly to the Ti-solution. The molar ratio of EDTA to total metal cations concentration EDTA/M was important and chosen at unity, the cation ratios of Ba:Sm:Ti are 6:14:27.

With the dissolution of $BaCO_3$ powder and the evolution of CO_2 gases, the solution became transparent. The solution, while stirred with a magnetic stirrer, was heated further at 140 °C for 1–2 h until the solution viscosity became so high that stirring became impossible. The solution became transparent gel and then deep brown resin. Throughout the process, no signs of precipitation were observed. Then the sample beaker was removed from the hot plate and placed into an oven immediately to char the resin at 230 °C for 30 min. The resin precursor was formed and then ground to coarse particles. Finally, the precursors were calcined at 700–1100 °C for 3 h to obtain the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) powders. The procedure used to prepare $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) powders by the sol–gel process is shown in Fig. 1.

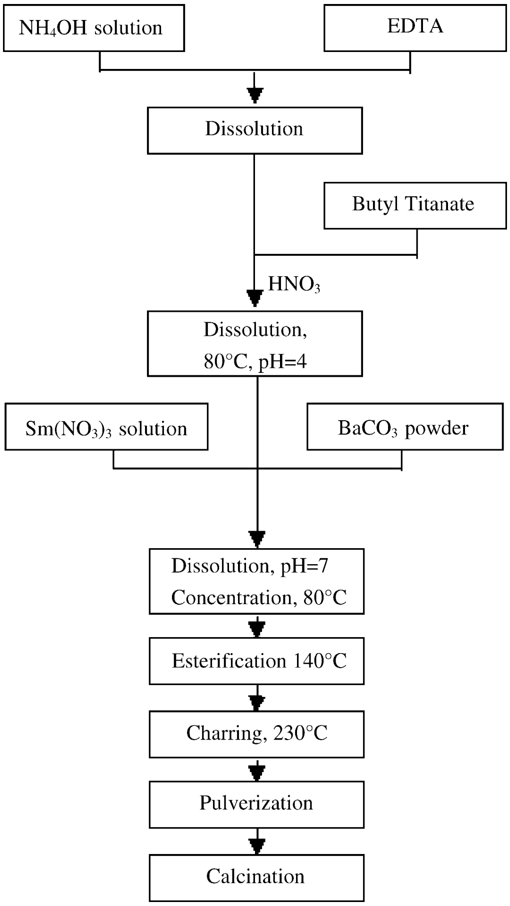

Fig. 1. Flow chart for the preparation of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powders.

The $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) powders calcined at 1000 °C for 3 h were added with organic binder, passed through a mesh and pressed into disks 12 mm in diameter and 4–6 mm thickness at a pressure of 100 MPa. The disks were sintered in air at 1350–1360 °C for 3 h. A part of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) powders calcined at 1000 °C for 3 h were ball milled in ethanol using zirconia media for 24 h and were also used for sintering study.

The pyrolysis and decomposition behavior of precursors were monitored by differential thermal analysis (DTA) and thermogravimetric (TG) analysis up to 1000 °C at a heating rate of 10 °C/min under nitrogen atmosphere. The crystalline phases of the samples were identified with X-ray diffraction (XRD) analysis using monochromatic Cu Kα radiation. The particle size and morphology of powder were examined with a scanning electron microscope (SEM).

The dielectric constants and unloaded Q values at microwave frequency were measured in the $TE_{01\delta}$ dielectric resonator mode using the Hakki and Coleman method [13].

3. Results and discussion

The differential thermal analysis (DTA) and thermogravimetric (TG) analysis for the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) precursor are shown in Fig. 2. The endothermic peak in the DTA curve around 64.5 °C, corresponding to the weight loss shown by TG, is due to the dehydration of the precursor. The exothermic peaks around 366.7 °C, its satellite peak at 388.9 and 499.6 °C, accompanied by the first sharp weight loss, is due to the breakup of EDTA compounds into carbonates and nitrates, volatilization of NH_4NO_3 and the elimination of residual CO_3^{2-}, NO_3^{-}. The exothermic peak around 605.1 °C, is associate with the decomposition into the oxide and this reaction led to the occurrence of weight loss found in the TG curve. This is confirmed by calcination experiments. When the precursors are heated at 500 °C for 4 h, powders with a light brown tinge are obtained. It is clear that there are some residual organics in the powders still. Increasing the heating temperature to 600 °C, the powders become yellow ochre in color. The TG curve also shows that the decomposition of the precursor has almost no weight change after 800 °C.

The XRD patterns of the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) precursor calcined at 700–1100 °C in air for 3 h are

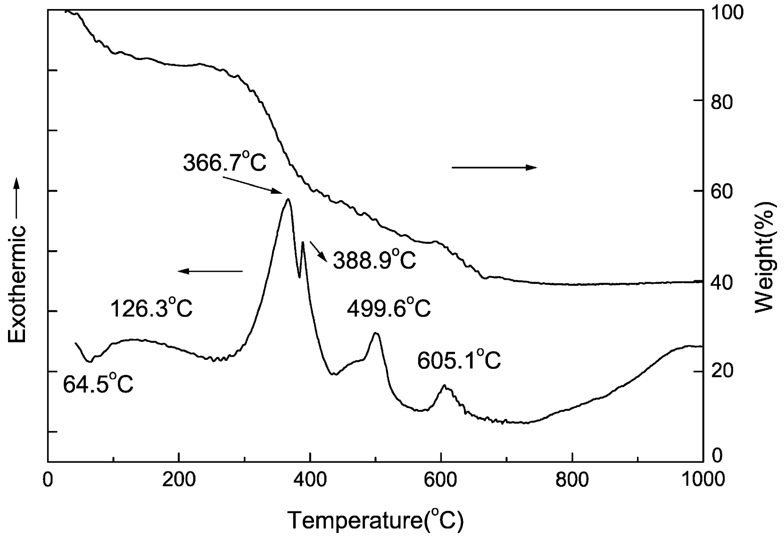

Fig. 2. TG and DTA curves for $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) precursor.

shown in Fig. 3. The powders obtained after heating up to 700 °C is amorphous. Heating the precursors at 850 °C for 3 h, powders start to crystallize and a mixture of $Sm_2Ti_2O_7$ with a pyrochlore-type cubic structure and $SmTiO_3$ is obtained where $Sm_2Ti_2O_7$ is major phase. Increasing the calcinations temperature to 900 °C, $Sm_2Ti_2O_7$ is still major phase, but $SmTiO_3$ phase disappears and the diffraction peaks from $BaTi_2O_5$ phase can be identified. At 950 °C, the products are the mixtures of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) with $Sm_2Ti_2O_7$ and $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) becomes major phase. Calcined the precursors 3 h at 1000 °C, the main reflection of $Sm_2Ti_2O_7$ at 30.3° almost cannot be observed because of its overlap with the (3 2 0) peak at 30.1° and (2 4 0) peak at 30.5° of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$). For the powder calcined at 1100 °C for 3 h, the XRD pattern is in excellent accord with that in reference [2,5,6,14] and JCPDS card 44-62, indicating X-ray single phase $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) formed. When the solid-state reaction method was used to synthesize $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, $Sm_2Ti_2O_7$ was still the major phase at the calcination temperature 1100 °C [5,6]. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ was synthesized via wet chemical method by Takahashi and Ikegami [7] and Hoffmann and Wagner [8], but the phase transformation as a function of temperature was not reported.

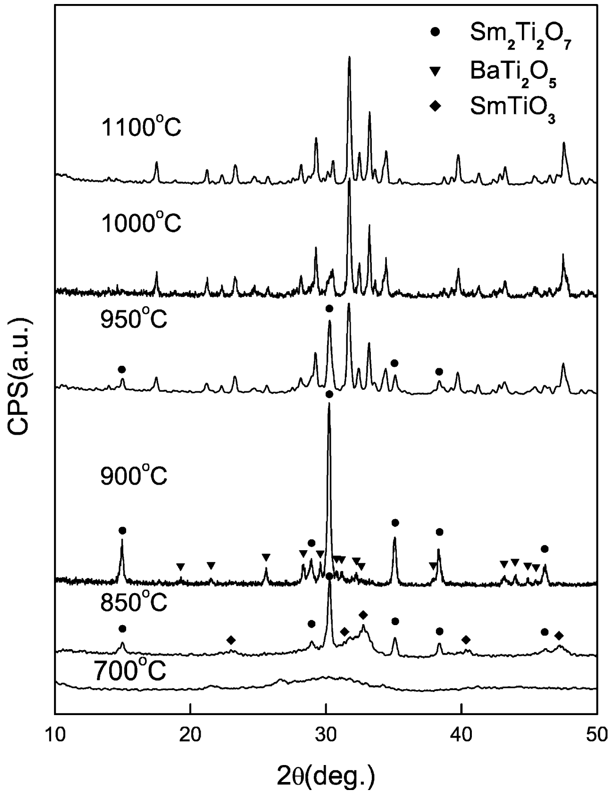

Fig. 3. XRD patterns of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) precursor after calcined at various temperatures for 3 h.

The SEM micrographs of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) precursor calcined at 900 and 1000 °C for 3 h are shown in Fig. 4. The powders are found to be agglomerates of very small particles.

sThe microwave dielectric properties of sintered $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) are summarized in Table 1. Since the Q shows frequency dependency, for comparison, the Q values in Table 1 are normalized using the relation $Q_f = \text{constant}$ [15], where f is the resonant frequency. The dielectric constant ε and Q_f of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) is in the range of 79.3–81.7 and 8850–11,330 GHz, respectively, which is consistent with that prepared with the solid-state reaction method [3,4]. Increasing the sintering temperature from 1350 to 1360 °C, Q_f of sintered $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics increases. On the other hand, ball-milling improved the Q_f of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$

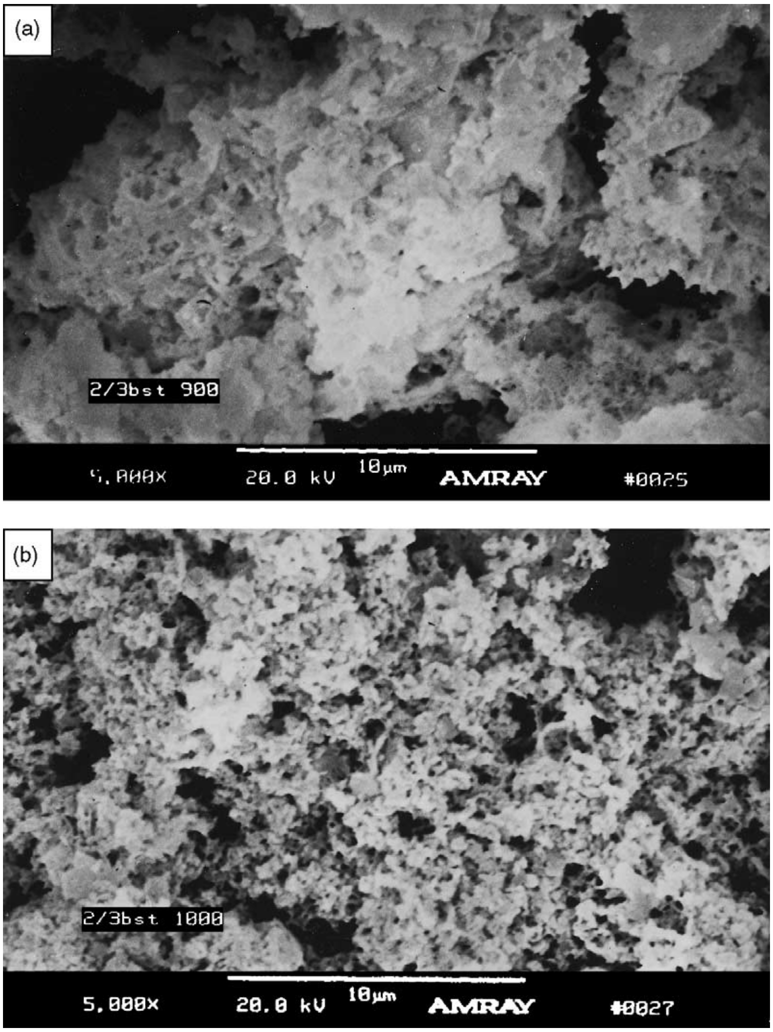

Fig. 4. SEM micrographs of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) powders. (a) 900 °C, 3 h; (b) 1000 °C, 3 h.

($x = 2/3$) ceramics, which could be attribute to the deagglomeration and improved mixing effects of ball-milling.

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics sintered at 1360 °C for 3 h showed the best microwave dielectric characteristics: $\varepsilon = 80.8$ and $Q_f = 11{,}330$ GHz, i.e. better than that prepared by the solid-state reaction method ($\varepsilon = 81$, $Q_f = 10{,}549$ GHz) at 1460 °C for 2 h [3,4].

Table 1
Microwave dielectric characteristics of the sintered $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$)

Ball milling	Sintering temperature (°C)	f (GHz)	ε	Q_f (GHz)
No	1350	4.56	81.1	8850
No	1350	4.35	79.3	8900
No	1360	5.65	81.1	9880
No	1360	4.66	80.8	9610
No	1360	4.53	80.4	9100
Yes	1350	4.36	81.1	9640
Yes	1360	4.06	80.8	11330
Yes	1360	4.72	81.3	10690
Yes	1360	4.25	81.7	10810

4. Conclusion

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ powders were prepared by a sol–gel method using ethylenediaminetetraacetic acids as a complexing agent. The microwave dielectric properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics sintered at different temperatures were evaluated. Ball-milling improved the microwave dielectric properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 2/3$) ceramics obtained at 1360 °C for 3 h showed excellent microwave dielectric properties: $\varepsilon = 80.8$ and $Q_f = 11{,}330$ GHz, which are better than that prepared by the conventional solid-state reaction method at 1460 °C for 2 h.

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