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Polymeric precursor synthesis of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powder

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Abstract

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powders were synthesized by the polymeric precursor method using ethylenediaminetetraacetic acids as chelating agent and ethanol glycol as esterification agent. DTA-TG, XRD and SEM were used to characterize the precursors and derived oxide powders. Powders calcined at 700 °C were found to be amorphous, but well-crystallized $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ was obtained at temperature of 1000 °C for 3 h with the primary size of about 100–200 nm. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

Ceramics based on $BaO–Ln_2O_3–TiO_2$ (Ln = Sm, Nd) are designed into circuits for numerous wireless applications below 5 GHz. They have high dielectric constant in the 80–90 range, modest quality factor Q (1.5–4 K, ~3 GHz) and low temperature coefficient of resonant frequency [1–6]. Compared with $BaO–Nd_2O_3–TiO_2$ system, $BaO–Sm_2O_3–TiO_2$ system ceramics has higher Q and slight lower dielectric constant so that it attracted many researchers. An especially interesting part of the phase diagram is the solid solution region with general formula $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ [1,5–7]. It is reported that the solid solution with x close to 2/3 has the best microwave dielectric properties [1].

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 inhabits the compositional and microstructural homogeneity of sintered products. In order to overcome these drawbacks, wet chemical methods [8,9] have been developed for the synthesis of pure, single-phase mixed oxide powders with controlled powder characteristics. Some researchers reported the wet chemical synthesis of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics [10,11]. An improved coprecipitation method[10] was used to prepare $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x = 0.5$) powders and ceramics. Hoffmann and Waser [11] 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. In this paper, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ is prepared by a polymeric precursor method using ethylenediaminetetraacetic acid as a cheleating agent and ethylene glycol as esterification agent [12,13].

2. Experimental

Nd_2O_3, nitric acid, butyl titanate ($Ti(OC_4H_9)_4$), $BaCO_3$ powder, ethylene glycol and EDTA were employed as the starting ingredients. All chemicals were reagent grade and used as received. Butyl titanate was added into ethylene glycol followed by the addition of EDTA, then enough ammonium hydroxide and distilled water was added to adjust the pH of the solution to 7. The opaque, white solution was heated at 80 °C with continuous stirring. $Sm(NO_3)_3$ solution (Sm_2O_3 powder dissolved into nitric acid) and $BaCO_3$ powder were added when the solution became a clear, light yellow color. The molar ratio of EDTA to total metal cations concentration EDTA/M was kept at unity [12,13], the molar ratio of EG to EDTA was 4, and the cation ratios of Ba:Sm:Ti = 6:14:27.

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With the dissolution of $BaCO_3$ powder and the evolution of CO_2 gases, the solution became a transparent, clear, yellow color. With continued heating at 80 °C to evaporate superfluous water, the solution became a transparent gel with high viscosity. The viscous mass, while stirred with a magnetic stirrer, was heated further for 2–4 h at 140 °C. Throughout the process, no signs of precipitation were observed. Then the sample was removed from the hot plate and placed into an oven (preheated to 230 °C) immediately to char the resin for 30 min. The resins expanded rapidly and finally formed dry sponge. The apparent volume increased for about 30–50 times after charring and the resin became very loose This solid resin precursor was pulverized and then calcined at 700–1000 °C for 3 h to obtain the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) ceramic powders. The yellow powders were passed through 120 mesh for analysis. The procedure used to prepare $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) powders by the polymeric precursor method is shown in Fig. 1.

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 10C/min under nitrogen atmosphere. The crystalline phases of the samples were identified with X-ray diffraction (XRD) analysis using monochromatic CuK_{α} radiation. The particle size and morphology of powder were examined with a scanning electron microscopy (SEM).

3. Results and discussion

The differential thermal analysis (DTA) and thermogravimetric (TG) analysis for the $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) precursor are shown in Fig. 2. The endothermic peak in the DTA curve around 64.7 °C, corresponding to the weight loss shown by TG, is due to the dehydration of the precursor. The exothermic peaks around 370 and 409.3 °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 largest exothermic peak around 523.1 °C and its satellite peak at 477.8 °C in the DTA curves are due to the decomposition into the oxide.

The XRD patterns of the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) precursor calcined at 700–1000 °C in air for 3 h are shown in Fig. 3. The powders obtained after heating up to 700 °C is almost X-ray amorphous and only small broaden peaks appear. At 850 °C powders start to crystallize but the major phase is $Sm_2Ti_2O_7$ with a pyrochlore-type cubic structure, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) phase (trace) also appears. Increasing the calcination temperature to 900 °C, $Sm_2Ti_2O_7$ is still major phase along with $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) and minor amount of $BaTi_2O_5$. Pure $BaTi_2O_5$ phase could not be obtained by solid-state reaction method [14–16]. $BaTi_2O_5$ phase forms only by crystallization from a

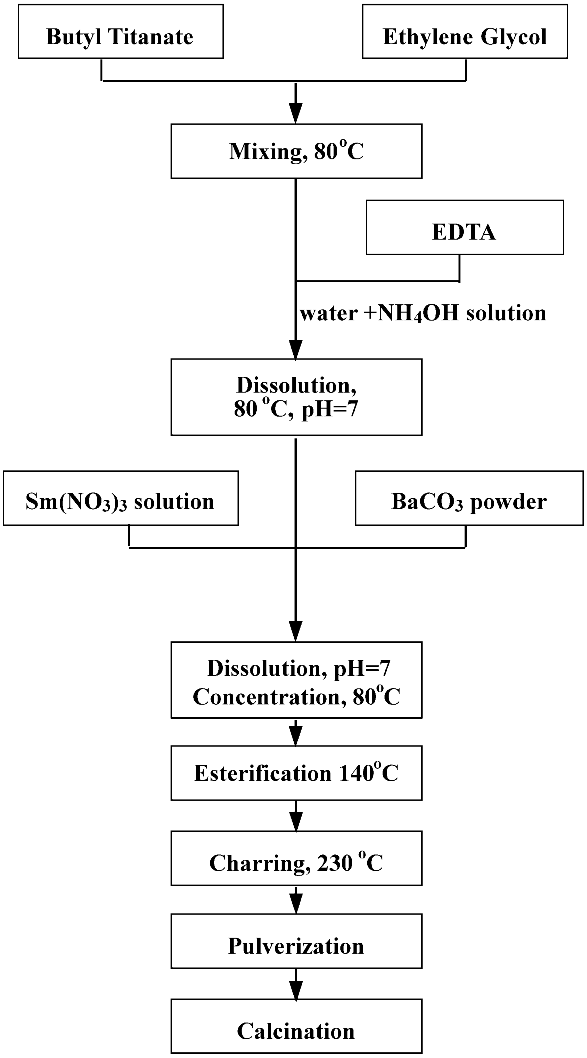

Fig. 1. Flow chart for the preparation of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powders.

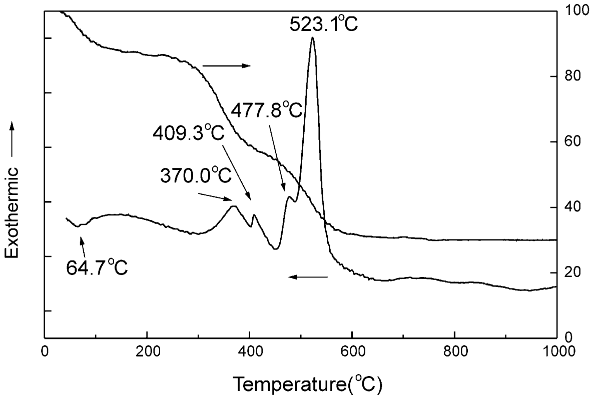

Fig. 2. TG and DTA curves for $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) precursor.

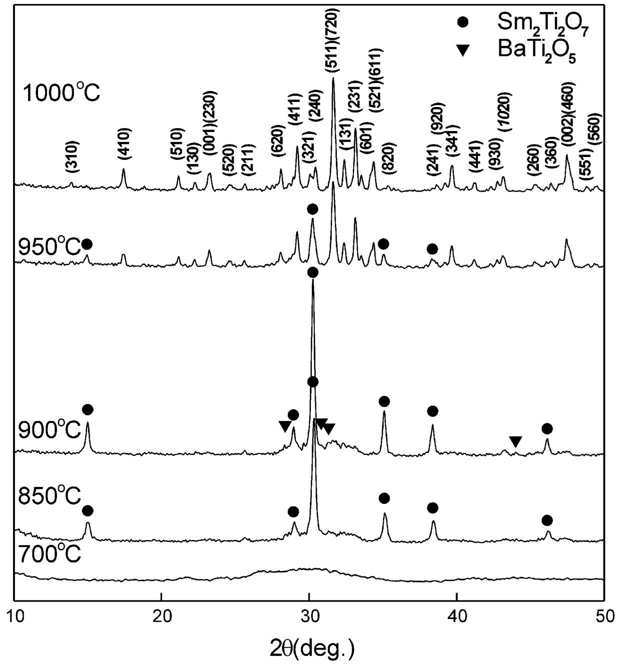

Fig. 3. XRD patterns of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) precursor after calcined at various temperatures for 3 h.

liquid phase and has lower temperature stability at ~1210 °C [14]. The sol–gel synthesis of $BaTi_2O_5$ has also been reported and this compound began to form at 700 °C [17,18]. Obviously, $BaTi_2O_5$ phase formed at 900 °C in present work is consistent with that in literatures. Calcined precursor 3 h at 950 °C, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) become major phase but $Sm_2Ti_2O_7$ diffraction peaks are still remained where $BaTi_2O_5$ phase is not observed. At 1000 °C, $Sm_2Ti_2O_7$ diffraction peaks are no longer distinguishable and the XRD pattern is in excellent accord with that in reference [2–4] 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 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 calcination temperature 1100 °C [3,4]. In addition, $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ has also been synthesized by this polymeric precursor method [12], but single phase $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ formed at 900 °C and no any intermediate phase appeared during the process. The reason for different results is due to the difference of radii between Nd^{3+} and Sm^{3+} and $Sm_2Ti_2O_7$ with a pyrochlore-type cubic structure can be formed more easily than $Nd_2Ti_2O_7$ with a perovskite-type structure. $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ was synthesized by wet chemical method in Refs. [10] and [11], but the phase transformation as a function of temperature was not reported. We cannot determine the temperature that single phase $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ formed.

The SEM micrographs of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) precursor calcined at 1000 °C for 3 h are shown in Fig. 4. The powders are found to be agglomerates of very small particles and the primary particles are about 100–200 nm in size.

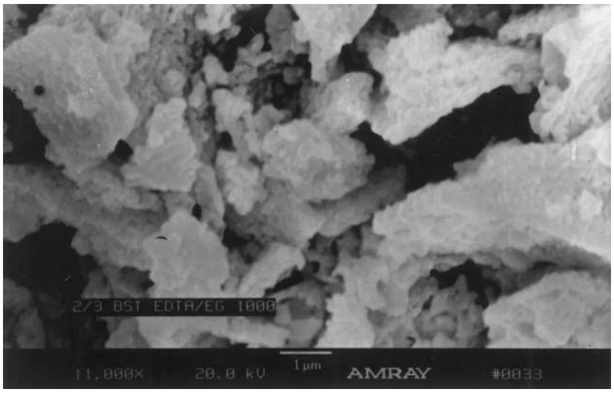

Fig. 4. SEM micrographs of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) powders (1000 °C, 3 h).

The $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) powder calcined at 1000 °C for 3 h was pressed under a pressure of 98 MPa into discs (12 mm in diameter and 6 mm thick) and sintered in air at 1350 and 1360 °C for 3 h. The apparent density of the sintered pellets is determined by measuring the weight and dimensions. The density is 5.69 and 5.74 g/cm^3 for the pellets sintered at 1350 and 1360 °C respectively, corresponding to 96.6 and 97.5% theoretical, respectively. The microwave dielectric properties of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics derived from EDTA precursor will be measured in our further work.

This polymeric precursor process involves the ability of EDTA to form polybasic acid chelates with various cations from elements such as Ti, Ba and Sm. These chelates can undergo polyesterification when heated in a polyhydroxyl alcohol (ethylene glycol) to form a polymeric glass which has the cations uniformly distributed throughout [9,13]. Therefore, no sign of precipitation or crystallization was observed during concentration and polymerization in our experiment. Thus the glass retains homogeneity on the atomic scale and may be calcined to yield fine particulate oxides whose chemistry has been precisely controlled.

4. Conclusion

$Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ powders were synthesized by polymeric precursor method using ethylenediaminetetraacetic acids as chelating agent and ethanol glycol as esterification agent. Well-crystallized $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ was obtained at temperature of 1000 °C for 3 h, and the primary size is about 100–200 nm. The formation of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ through the chemical route can be attributed to the homogenous distribution of cations.

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