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Synthesis of pure $Ba(Mg_{1/3}Ta_{2/3})O_3$ microwave dielectric powder by citrate gel-processing route

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Abstract

A new citrate gel-processing route to synthesize pure BMT powder at low temperature (600°C) along with the XRD, SEM and DTA results are reported. Ta-citrate was adopted as the starting precursor. For comparison, the conventional approach using high purity Ta_2O_3 powder was also used as starting material to prepare BMT powder. It was discovered that a pure BMT phase, using the sol–gel route, with pseudocubic perovskite structure was formed at much lower temperature (600°C) and with nano-particle size powder (100–200 nm), whereas, the synthesizing temperature for conventionally prepared powder was more than 1250°C. © 1998 Elsevier Science B.V.

Keywords: Microwave dielectrics; $Ba(Mg_{1/3}Ta_{2/3})O_3$; Citrate sol-gel synthesis; Thermogravimetric analysis; X-ray diffraction

1. Introduction

Since the ceramic material with the composition $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) was reported to have an extremely high Q value, many scientists have been attracted to study it [1–8]. However, a significant problem concerning the BMT ceramics using powders prepared by the conventional solid-state reaction method is their poor sinterability because of the presence of a secondary phase, such as $Ba_5Ta_4O_{15}$ and $Ba_4Ta_2O_9$ [2]. In general, phase impurities or sintering aids are expected to degrade the loss quality. Thus, pure BMT with homogeneous composition is essential to obtain high Q dielectrics. Many efforts have been made to try to create pure dense BMT ceramics. Matsumoto and Hiuga proposed a fast heating process [1], Chen et al. reported a process consisting of many repeated calcinations at high temperature (1300°C) [2] and Tochi reported a two-step synthesizing route via $BaCO_3$ and $MgTa_2O_6$ [3]. However, these techniques still require high firing temperatures of ~ 1600°C because of the low reactivity of BMT powder synthesized by conventional solid-state reaction which needs high temperatures (> 1250°C) and long reaction times (> 5 h).

Some chemical processes, which can provide high reactive oxides, as well as high purity and homogeneity, have been used for the preparation of BMT powders with high sinterability [4–8]. However, as for the coprecipitation method, it is almost impossible to precipitate all the cations quantitatively and simultaneously without segregation of any of the constituents into the precipitates. In general, the sol–gel process based upon hydrolysis of metal alkoxides need long refluxing time and gas protection [5–8]. Furthermore, the precursors such as tanta-

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lum alkoxide and $TaCl_5$, being used in these methods, are expensive and unstable and thus impractical from the industry point-of-view.

The citrate gel process is thought to be highly promising for achieving homogeneous mixing of the component cations on the atomic scale and has the potential advantage over the above methods; it is easy to operate and offer much saving in processing time. This process was originally used to obtain highly dispersed mixed oxides or oxide solid solutions of perovskites, spinets and garnets [9–13]. The technique was later developed for high temperature superconducting oxides by many research groups [14–17]. It is considered that both the citrate: metal ration and the pH value of the initial solution are most important to obtain a clear gel with no precipitation. However, there are no previous reports, to the best of our knowledge, on the synthesis of pure BMT powder by the citrate gel process.

In this paper, a citrate gel processing route to synthesize pure BMT powder at low temperature is given and investigated by use of XRD, DTA, TGA, TEM and SEM methods. Our self-prepared Ta-citrate was adopted as the starting precursor.

2. Experimental

We prepared tantalum citrate, barium citrate and magnesium citrate solutions for use as starting materials. A schematic of the preparation procedure for the formation of BMT gels and powder is shown in Fig. 1. The obtained gels were calcined at 4500–1000°C in air for 2 h in an alumina boat. For comparison, for the synthesis by the conventional approach, The materials $BaCO_3$ (99.9%), MgO (99.9%) and Ta_2O_5 (99.99%) were used as starting materials.

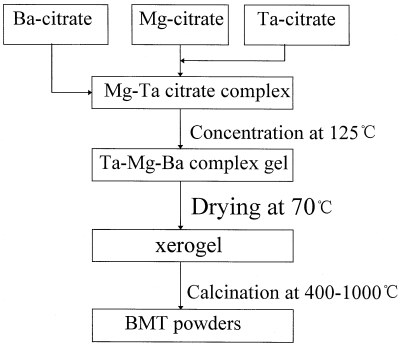

Fig. 1. Flow chart for the preparation of BMT powders by citrate-gel process.

X-ray diffraction (XRD) analysis using Cu$_{\alpha}$ radiation was carried out to evaluate the phase constitution. Differential thermal analysis (DTA) and thermogravimetry analysis (TGA) were carried out to understand the decomposition and synthesizing process. The morphology of the calcined powders was examined by scanning electron microscopy (SEM) and electron microscopy (TEM).

3. Results and discussion

As the Ta-citrate solution was dripped into the Ba, Mg-cirate mixed solution, a white colored colloidal suspension formed first, and then the PH of the solution was controlled using an ammonia–water solution. By stirring and heating at 100–130°C, a clear Ba, Mg, Ta citrate complex was obtained. Upon completion, the color began to change; at first a yellowish tint appeared indicating dehydration and then a highly viscous transparent gel was obtained directly, without the use of additional estering agents. The white colored precipitate is the Ba and Ta containing citrate complex, because it formed only when the Ba-citrate and Ta-citrate solutions were mixed together. The accurate chemical formula of the precipitate was identified by XRD analysis.

In order to optimize the synthetic conditions, DTA and TGA measurements were made and the results for the gel and mixed powder are shown in Fig. 2. From Fig. 2(a), a small endothermic peak at 147°C in the DTA curve was assigned to the melting point of citratric acid. The abrupt weight decrease at about 175°C, which also corresponds to a large and broad endothermic DTA peak, might be due to competing reactions corresponding to vaporization and the dehydration and decarboxylation of the citric acid. The exothermic peak at 350°C might be due to the combustion of itaconic anhydride in air [18] and the decomposition of tantalum and barium citrate into Ta_2O_5 and $BaCO_3$. Another exothermic peak at 480°C might correspond to the synthesis of BMT.

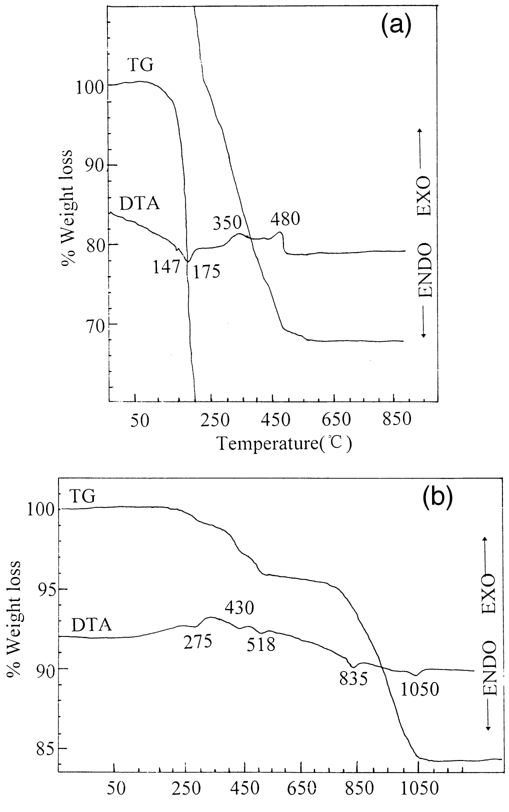

Fig. 2. (a) Differential thermal analysis (DTA) and thermogravimetric (TGA) curves (heating rate 2°C/min) for the BMT gel product. (b) Differential thermal analysis (DTA) and thermogravimetric (TGA) curves (heating rate 10°C/min) for the ball-milled mixed BMT powder.

The slight weight loss between 480°C and 590°C is due to the release of a small amount of residual fine ash of brown-gray color.

The DTA and TGA results for the conventional ball-milled mixed powder is shown in Fig. 2(b). Three small and broad endothermic DTA peaks from 275°C to 518°C, associated with total of about 4 wt% loss in the TGA, are obviously due to the release of OH and CO_2 associated with the MgO. About 11 wt% loss in TGA, which corresponds to an endothermic DTA peak at 835°C, appears to be associated with the decomposition of $BaCO_3$ and the form of $BaTa_2O_6$. Another endothermic peak at 1050°C appears to be due to the formation of BMT.

Fig. 3 shows the XRD patterns of BMT powders calcined at various temperatures in air for 2 h and composed to the spectra of Ta_2O_5 and $BaCO_3$. The latter were detected in the XRD pattern of BMT gel calcined at 400°C. A small amount of the complex perovskite BMT phase is present in the 400°C sample. $BaTa_2O_6$ begins to form at 500°C, and a completely pure BMT phase was obtained at 600°C for the samples prepared by the citrate gel-process (Fig. 3(a)). Whereas, for the conventional ball-milled mixed powder calcined at 1250°C for 2 h, there is still a small amount of $BaTa_2O_6$ present, indicated by the XRD pattern (Fig. 3(b)). This indicates that the intermediate $BaTa_2O_6$ phase appeared during the two synthesizing processes. But the synthesizing temperature for pure BMT powder prepared by present sol-gel process is much lower than for the conventional material.

The scanning electron micrographs were obtained to estimating the particle size and morphology (Fig.

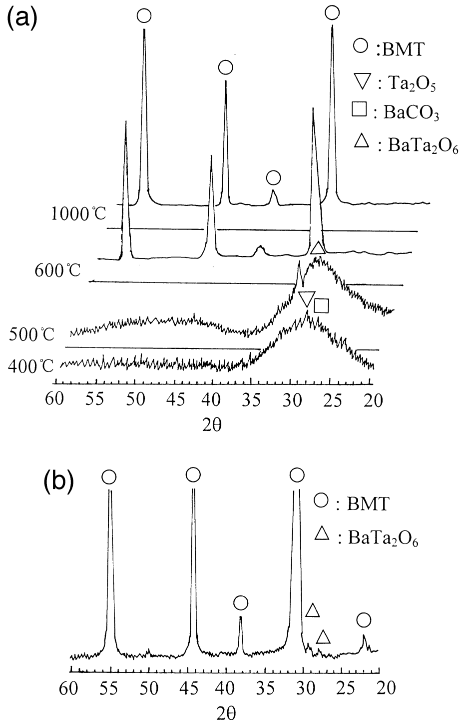

Fig. 3. (a) X-ray diffraction spectra of the BMT powder after heating the gel product at different temperatures for 2 h. (b) X-ray diffraction pattern of the BMT powder after heating the ball-milled mixed powder at 1250°C for 2 h.

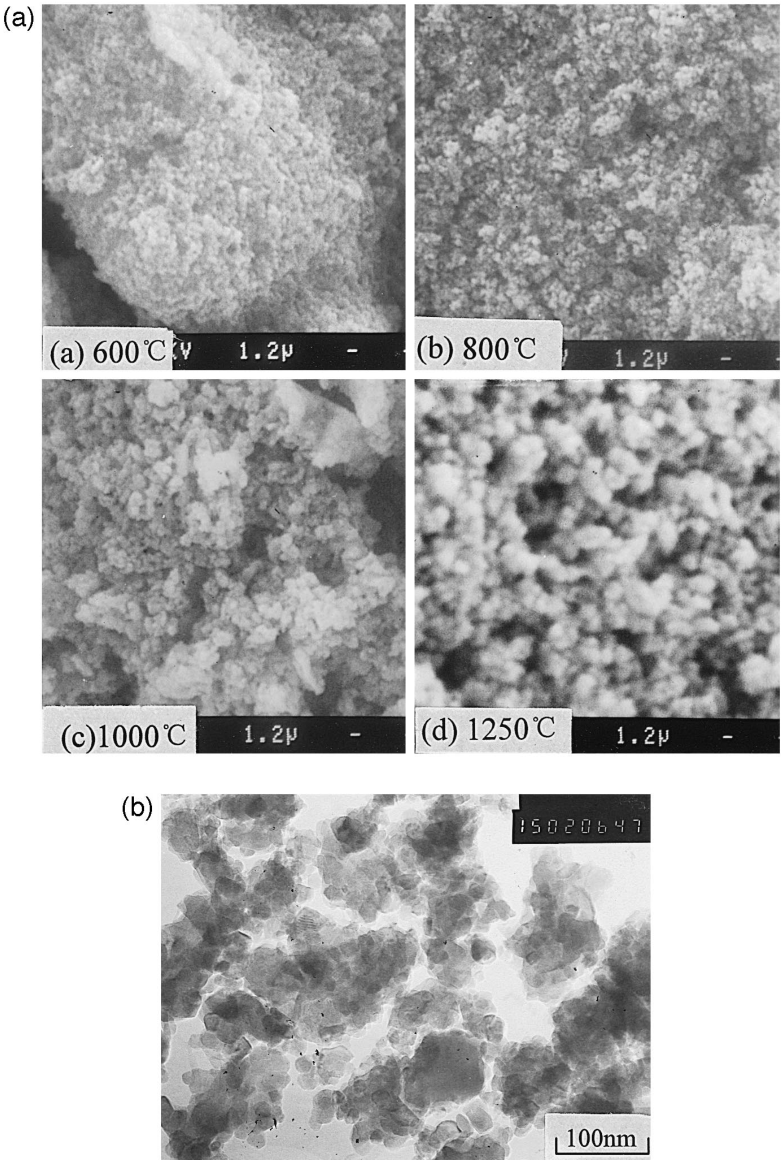

Fig. 4. Scanning electron micrographs of BMT powders calcined at different temperatures for 2 h. (a), (b), (c) prepared by citrate gel-process and (d) prepared by conventional process.

4(a)). The powder prepared by the sol–gel method and calcined at 600°C for 2 h consists of very fine particles and heavily agglomerated (panel (a)). But the powder calcined at 800°C for 2 h consists of nearly a homogenous particle size with small number of agglomerates (panel (b)). This result might be due to the release of small amount of residual carbon as CO_2 and a decrease in the amount of hydrogen bond as H_2O with the increase of calcining temperature. The TEM micrograph of the BMT powder fired at 800°C for 2 h is shown in Fig. 4(b). It indicates that the particle size is about 10–20 nm and the size of agglomerate to be about 100–200 nm.

Because BMT powders with high phase purity can be synthesized at a much lower temperature, around 600°C, by using powders derived from the citrate gel-process, and possessing much finer particle size than that obtained by the conventional process (Fig. 4(a), panel (d)), should show excellent sinterability.

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