



Nanocomposite Versus Sol-Gel Processing of Barium Magnesium Tantalate

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Abstract. Barium magnesium tantalate, $\text{Ba}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$ (BMT) was prepared by a nanocomposite processing route. Density, particle size and microstructure were determined on the BMT nanocomposite pellets sintered at various temperatures and compared with those derived from a sol-gel process. BMT ceramics prepared by the nanocomposite process showed fine grains of about $2\ \mu\text{m}$ and higher densities compared to that of BMT prepared by sol-gel processing, apparently due to a decreased temperature interval between crystallization and densification in the nanocomposite process.

Keywords: nanocomposite, sol-gel, barium magnesium tantalate

Introduction

Ceramics of perovskite oxides with general formula $\text{A}(\text{B}_{1/3}\text{B}_{2/3})\text{O}_3$ ($\text{A} = \text{Ba}$ ion, $\text{B}_1 = \text{Mg}$, Zn and $\text{B}_2 = \text{Ta}$, Nb) normally possessing a hexagonal superstructure (1:2 ordering of B_1 and B_2) have been extensively investigated for their excellent microwave dielectric properties [1–3]. Over the years, this material has been prepared by conventional methods [3] and oxine method [4]. However, BaTa_2O_6 forms as an intermediate product [4] in conventional methods due to repeated calcination and grinding steps and therefore, much higher heating schedules are required to obtain the single phase BMT [7]. It was reported that a dense ceramic of BMT is not obtained even if the sintering is carried out at 1600°C in air by conventional processing [3]. Sintering additives such as Mn^{2+} or Sn^{3+} or rapid sintering methods have been used to obtain dense ceramics with good microwave properties [5,6]. In the oxine method, the evaporation of magnesium-oxine chelate during thermal decomposition may pose a problem [4].

In recent years the sol-gel method has been used to synthesize BMT ceramic powders [7,8] and thin films [9] using metal alkoxide precursors. There is no doubt that this method offers the potential for low

temperature processing, better chemical homogeneity and improved microstructures especially for thin films. However, the special handling of extremely moisture sensitive metal alkoxide precursors and longer heating schedules of around 24 h [7] preclude the adoption of this technique for routine ceramic synthesis. Nanocomposites have been shown to exhibit superior properties as compared to single phases of the same composition prepared by sol-gel method [10–13].

In view of the above, we present an alternative low temperature method to synthesize phase pure, dense BMT ceramics without any additives by a nanocomposite approach during which wet mixing of the precursor powder is achieved in a slurry at a nano level. Also contamination due to undesirable phases like BaTa_2O_6 can be reduced to a lower level by mixing on a nanoscale. The objective of this work is to apply the principle of the sol-gel technique of mixing expensive precursors at the molecular level to inexpensive nanocomposite processing of mixing at a nano level to make the process simple. Thus this paper presents results on the nanocomposite versus sol-gel processing of BMT powders, their sinterabilities and corresponding microstructures.

Experimental Procedure

The experimental procedure adopted for the synthesis of BMT by sol-gel approach is depicted in Fig. 1. Barium metal (99%), magnesium ethoxide $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (98%) and tantalum (v) ethoxide $\text{Ta}(\text{OC}_2\text{H}_5)_5$ (99.8%) were used (all Aldrich Company) in this process. Initially a stoichiometric amount of tantalum (v) ethoxide was dissolved in 2-methoxy ethanol (2-MOE) in a flask and refluxed at 125°C for 8 h in argon atmosphere. The required amount of magnesium ethoxide was dissolved in 2-MOE and the solution was refluxed at 125°C for 6 h in argon atmosphere. A double alkoxide of tantalum and magnesium was apparently formed by mixing Ta and Mg precursor solutions.

Finally Ba metal was dissolved in 2-MOE in a separate flask and refluxed at 125°C for 8 h. This Ba precursor solution was cooled to room temperature and then added to the Ta-Mg double alkoxide solution and this solution was refluxed at 125°C for 8 h to

obtain a clear Ba-Mg-Ta precursor solution. By adding concentrated nitric acid, the pH of the resulting BMT precursor solution was adjusted to 10 from a starting pH of 13. Then the solution was hydrolyzed by adding 1:4 ratio of water and 2-MOE at a slow rate in order to obtain a homogeneous BMT gel. The gel was dried at 60°C in air oven. The dried gel was crushed into powder with a mortar and pestle. The organics from the gel powder were removed by heating it at 600°C for 4 h. The powder was mixed with polyvinyl alcohol (PVA) as binder, pressed into pellets, binder burned out, and heated at different temperatures.

Figure 2 shows the nanocomposite approach in which barium carbonate (BaCO_3) of particle size in the range 0.3 to $2\ \mu\text{m}$ (nanophase powder is not available) (Fig. 3a) (Aldrich), ultrafine magnesium oxide (MgO) of particle size of less than 50 nm (Fig. 3b) (supplied by UBE Industries, Japan) and tantalum oxide (Ta_2O_5) fine powder (Johnson Matthey) of particle size of 200 nm (Fig. 3c) were used. Adsorbed water contents were determined from weight loss due

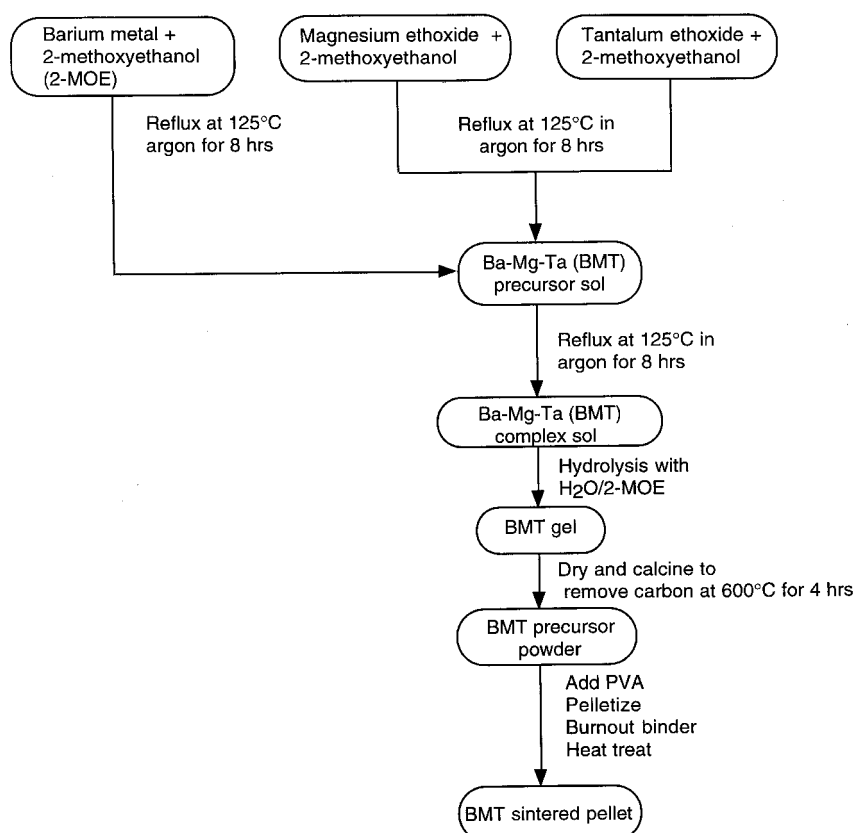


Fig. 1. Flow chart for the synthesis of barium magnesium tantalate (BMT) by sol-gel processing.

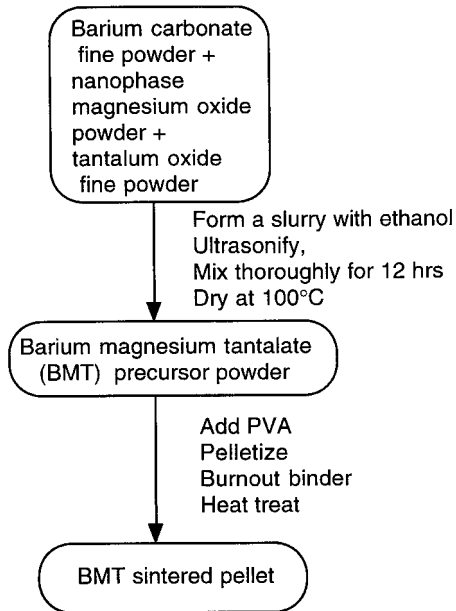


Fig. 2. Flow chart for the synthesis of barium magnesium tantalate (BMT) by nanocomposite processing.

to dehydration by heating at 600 °C for 1 h. Stoichiometric quantities of BaCO_3 , Ta_2O_5 and MgO were made into a slurry and ultrasonicated for 20 min with ethanol, stirred for about 12 h and dried at 100 °C in an oven to remove water. This presumably resulted in intimate mixing.

The gel powder heat treated at 600 °C for 4 h and the nanocomposite mixed powder dried at 100 °C were each mixed with 2 wt% polyvinyl alcohol (PVA) as binder and pressed into pellets using a pressure of 15000 psi. The pellets were sintered at 1450, 1500 and 1600 °C for 4 h to determine densification behavior. Phase identification was carried out using an X-ray diffractometer (Scintag model DMC 105) with copper K_α radiation. Microstructural studies were carried out on the sintered pellets with a scanning electron microscope (Model ISI-DS-130, Akashi Beam Technology Corporation, Japan).

Results and Discussion

The XRD patterns of BMT sol-gel powder heat treated at 600 °C for 4 h and the slurry mixed nanocomposite powder heat treated at 1350 °C for 4 h are shown in Fig. 4. While the sol-gel process needed only a temperature of 600 °C, the

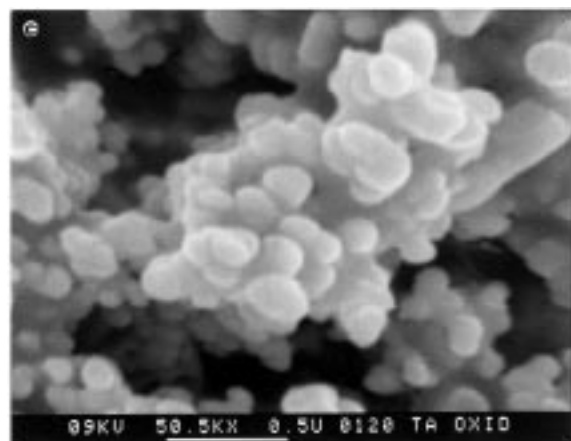
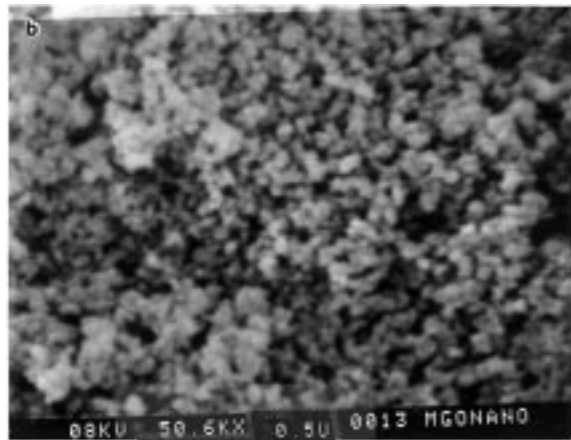
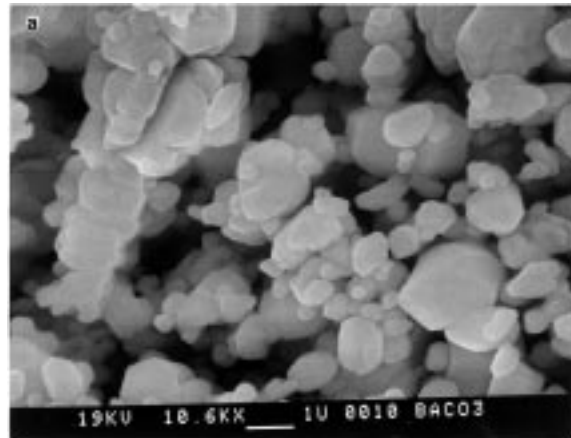


Fig. 3. Scanning electron micrographs of (a) BaCO_3 (b) MgO (c) Ta_2O_5 used in the nanocomposite processing.

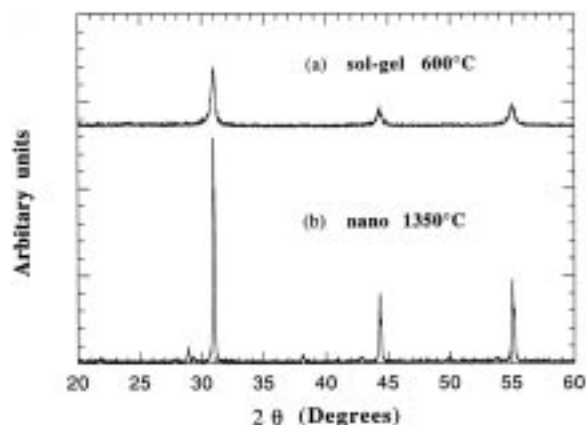


Fig. 4. XRD patterns of barium magnesium tantalate prepared (a) by sol-gel processing and by (b) nanocomposite processing.

nanocomposite powder needed 1350 °C for BMT crystallization. The XRD patterns indicate that, in sol-gel processing, phase pure and well crystallized BMT was obtained at a very low temperature of 600 °C. The XRD pattern is in agreement with JCPDS (Joint committee on powder diffraction standards) file number 18-176 for BMT. But in the case of nanocomposite approach, there is a small amount of second phase of BaTa_2O_6 even after heating at 1350 °C. This phase was previously observed to a much greater extent in traditional mixed oxide solid state processing [5].

The relative bulk densities (% theoretical) of these compacts sintered at different temperatures are shown in Fig. 5. It is clear from Fig. 5 that the pellets prepared by nanocomposite processing yielded better

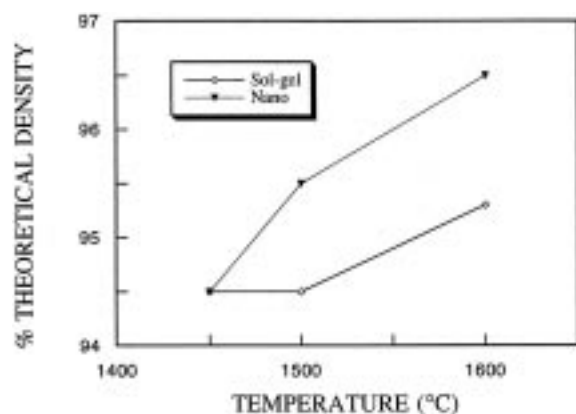


Fig. 5. Variation of relative bulk density (%theoretical) of nanocomposite and sol-gel derived pellets sintered at different temperatures (soaking time 4 h).

densities than the pellets prepared by sol-gel processing. Because crystallization and densification occur within a short temperature interval, nanocomposite processing led to better densification compared to sol-gel processing which underwent a calcining step that led to crystallization of the equilibrium phase [11]. Even though crystallization of sol-gel powder occurred at a lower temperature of 600 °C when compared with that of nanocomposite powder, the temperature interval between crystallization and sintering is high and hence densification can occur only at a relatively higher temperature in the sol-gel powder compared to nanocomposite mixed powder. When the equilibrium phase crystallizes, it is very difficult to densify and this is the case with sol-gel process. Scanning electron micrographs of BMT sol-gel powder and heat treated nanocomposite mixed powder are shown in Fig. 6. In the case of sol-gel powder heat treated at 600 °C for 4 h (Fig. 6a), a very fine particle size was observed with high agglomeration. The particle size of the powder calcined at 600 °C, was less than 0.1 μm. In nanocomposite powder heat treated at 1350 °C for 4 h the average particle size was approximately 0.2–0.3 μm (Fig. 6b). Figure 7 shows microstructures of thermally etched pellets sintered at 1500 °C for 4 h. Average grain size of about 2 μm was seen in nanocomposite approach while in sol-gel process, it was more than 4 μm. Some grains were greater than 5 μm in size in the sintered pellets made by sol-gel and this grain growth apparently led to a decrease in density. Increased grain growth in oxide ceramics such as mullite leads to low density because pores coalesce and gases are released [14–16] and this mechanism is presumably applicable to the BMT phase investigated here.

It is evident from the nanocomposite process that the precursor oxides can be easily handled in ordinary atmosphere. Higher density and fine grained ceramics were achieved by the nanocomposite process. In the case of the sol-gel process, the highly reactive metal alkoxide precursors should be handled in a glove box and this may add to the cost of preparation. Hence the present nanocomposite approach seems to be worth exploring for other systems as well.

Conclusions

We have prepared BMT by a nanocomposite route making use of inexpensive precursors and without

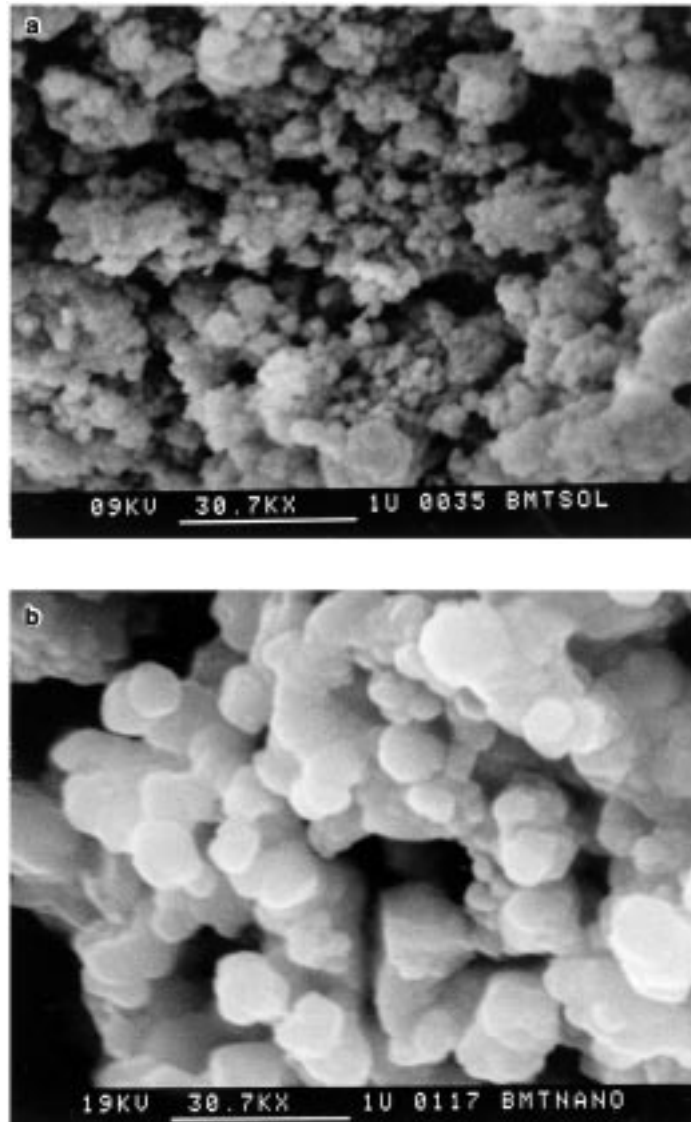


Fig. 6. Scanning electron micrographs of (a) BMT sol-gel powder heat treated at 600°C for 4 h and (b) nanocomposite powder heat treated at 1350°C for 4 h.

adding any sintering aids. Relatively higher density BMT ceramics were formed at 1600°C with shorter heating schedules (4 h) by the nanocomposite route when compared to sol-gel derived ceramics [7]. Due to the lower temperature interval between crystallization and densification, nanocomposite powder showed better sintering compared to sol-gel powder. SEM micrographs of heat treated (1350°C for 4 h) nanocomposite powder showed a particle size of $< 1 \mu\text{m}$. The present method eliminates intermediate

calcination, grinding steps and requires no special handling of precursors. The sol-gel approach, on the other hand, requires special handling of precursors and an intermediate calcination step.

Acknowledgments

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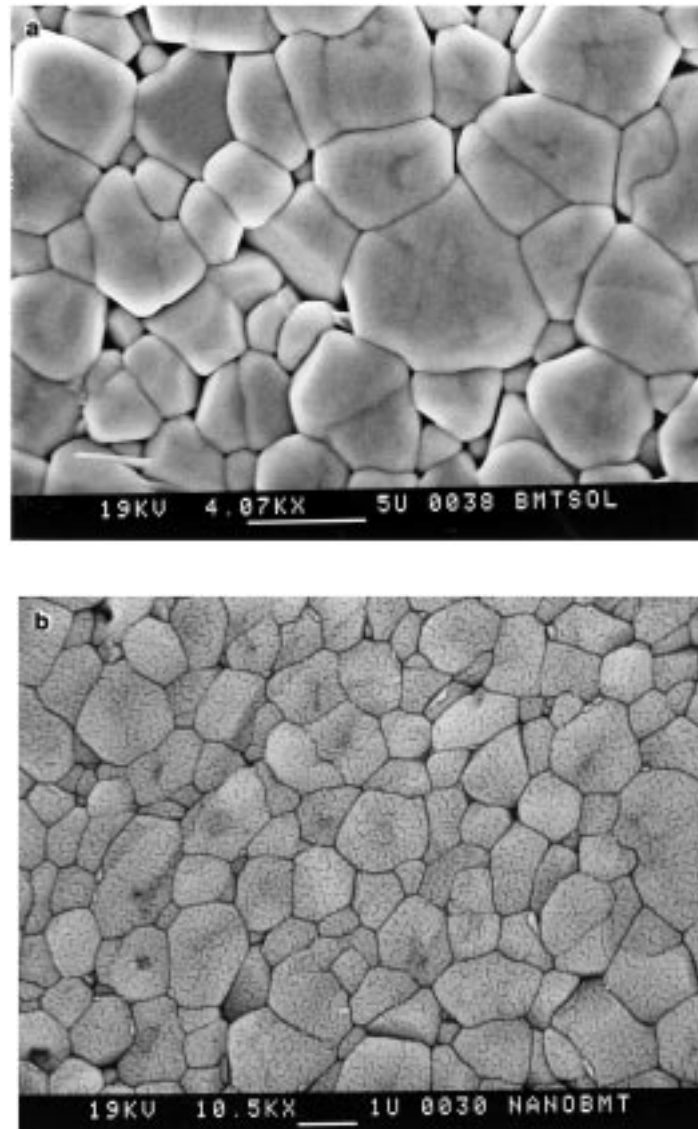


Fig. 7. Scanning electron micrographs of (a) sol-gel and (b) nanocomposite BMT pellets sintered at 1500 °C for 4 h.

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