

Auto-ignition synthesis of nanocrystalline BaTi₄O₉ powder

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Monophasic BaTi₄O₉ powder has been prepared by an auto-ignition route. The auto-ignition of the gel, prepared by thermal dehydration of a pH adjusted citrate–nitrate solution, directly resulted in voluminous BaTi₄O₉ powder with traces of carbonaceous material. Calcination of the voluminous powder at 600 °C produced pure nanocrystalline BaTi₄O₉ powder. Process parameters such as the amount of citric acid used for gelation and pH of the starting solution were found to have a significant influence on the gel stability, temperature required for the phase formation and the powder characteristics. TEM micrographs revealed the nanocrystalline nature (crystallite size < 50 nm) of the powder. BaTi₄O₉ powder when cold pressed and sintered at 1200 °C for 6 hours in air reached ≈ 96% of its theoretical density.

Introduction

BaTi₄O₉ is a low loss ($Q > 10000$), temperature stable ($\tau_f \approx 14 \text{ ppm K}^{-1}$) dielectric material with reasonably high dielectric constant ($\epsilon_r \approx 38$) and hence well suited for dielectric resonators used in the microwave communication technology.^{1,2} The fabrication of highly dense bodies of this material with high phase purity is of practical importance for obtaining the desired dielectric characteristics.

However, there are only a few reports available for the low temperature synthesis of monophasic BaTi₄O₉. Choy *et al.*³ successfully prepared monophasic BaTi₄O₉ powder by the pyrolysis of amorphous citrate gels at 1300 °C for 2 hours. Lin *et al.*⁴ obtained BaTi₄O₉ with a minority TiO₂ phase by a solid state reaction between BaCO₃ and TiO₂ at 1360 °C for 5 hours. The problems associated with solid state synthesis, *viz.* contamination from the grinding media and formation of unwanted phases can be successfully solved by using wet chemical processes such as co-precipitation, sol–gel and combustion. Among the available solution chemistry routes, the combustion technique is capable of producing nanocrystalline powders of oxide ceramics at lower calcination temperature in a surprisingly shorter time.^{5–7} The powder obtained by this technique generally has the highest degree of phase purity with improved powder characteristics such as narrow particle size distribution, higher surface area and better sinterability. The combustion technique involves an exothermic decomposition of a fuel–oxidant (*e.g.* citrate–nitrate, glycine–nitrate, urea–nitrate *etc.*) precursor which results in either a finely divided powder of the required phase or semi-decomposed precursor having a considerable carbonaceous residue depending on the nature of fuel and fuel-to-oxidant ratio used in the process.⁷

The formation of a viscous liquid or gel is a primary condition for an intimate blending of the starting constituents and prevention of random redox reactions between the fuel and the oxidant. The nature of the fuel, its amount and pH of the starting solution are some of the important process parameters for obtaining transparent viscous gels without any phase separation or precipitation. Purohit *et al.*⁸ and Oh *et al.*⁹ reported the crucial effect of the pH for stabilization of gels. The powder characteristics obtained by the combustion technique are primarily dependent on the enthalpy or the

flame temperature generated during the combustion, which itself is a function of the nature of the fuel and fuel-to-oxidant ratio used in the process.¹⁰

In this paper, the low temperature synthesis of nanocrystalline, monophasic BaTi₄O₉ powder through auto-ignition of the gel is reported. The effects of pH and amount of citric acid on the gel formation, its decomposition behavior and powder characteristics obtained were investigated. The BaTi₄O₉ powders obtained through this technique were characterized by X-ray diffraction (XRD), surface area analysis, scanning electron microscopy (SEM), transmission electron microscopy (TEM) and sinterability experiments.

Experimental

High purity TiO(NO₃)₂, Ba(NO₃)₂, citric acid (C₆H₈O₇·H₂O) and aqueous ammonia were used as the starting materials. TiO(NO₃)₂ was prepared by precipitating the TiCl₄ as hydrated titania using aqueous ammonia and dissolving the precipitate in a minimum volume of 1.4 M HNO₃ after complete washing of the chloride ions. The TiO(NO₃)₂ solution was analyzed gravimetrically as TiO₂ and found to contain *ca.* 0.16 mol l⁻¹ of titania. Ba(NO₃)₂ was dissolved in hot water and cooled to room temperature. The required volume of TiO(NO₃)₂ solution was added to a Ba(NO₃)₂ solution maintaining the Ba to Ti mol ratio at 1:4. Citric acid crystals were dissolved in the mixed metal nitrate and oxynitrate solution maintaining the total metal ions to citric acid molar ratio at 1:0.5 to obtain the citrate–nitrate solution. Dilute aqueous ammonia was added slowly into the citrate–nitrate solution to adjust the pH to ≈ 6. Thermal dehydration of the pH adjusted citrate–nitrate solutions to evaporate the excess solvent (at ≈ 80 °C on a hot plate), resulted in the highly viscous yellowish gel denoted as the precursor. As soon as this gel was formed, the temperature of the hot plate was raised to ≈ 225 °C. The gel then swelled and ignited with an evolution of a large volume of gaseous products. The auto-ignition, which lasted for about 5 seconds, resulted in a voluminous BaTi₄O₉ powder with a slight blackish tinge. 2 g of the powder led to a volume of 50 cm³ in the beaker *i.e.* the apparent density of the powder is ≈ 0.04 g cm⁻³. Owing to the high exothermicity and gas evolution associated with auto-ignition, the volume of the

beaker in which synthesis carried out was much larger than the volume of the precursor to avoid any damage and loss of powder to the surroundings. There must also be an arrangement for safe ventilation of the gases produced during auto-ignition. In the present study, 2 g of the powder could be safely produced in a 250 cm³ beaker under a fume hood. The powder obtained after auto-ignition was calcined at 600 °C for 2 hours to obtain pure, monophasic BaTi₄O₉ powder. To observe the effect of the amount of the fuel and pH on the gel stability, temperature required for the phase formation and powder characteristics; the process was repeated with varying total metal ions to citric acid molar ratio, with or without pH adjustment *i.e.*, 1:0.25 and 1:1 with pH adjustment and 1:2 without pH adjustment. The general flowchart for the process is shown in Fig. 1.

Simultaneous TG/DTA experiments were performed, using a SETARAM simultaneous TG/DTA instrument, Model 92-16.18, on part of the dried gel precursors in a flowing air atmosphere with a heating rate of 10 °C min⁻¹ to measure the minimum calcination temperature and the decomposition behaviour. X-Ray diffraction studies were carried out for phase identification of the powders obtained after auto-ignition, calcination and sintering. The patterns are reported in the range 2θ 25–35°, *i.e.*, the range in which most of the prominent peaks are observed, with a scan rate of 1° min⁻¹ using Cu-Kα radiation on a Philips X-ray diffractometer, Model PW 1927. The unit cell parameters were determined using a least-squares refinement program. The standard BET technique with N₂ adsorption was used for specific surface area analysis of the BaTi₄O₉ powders employing a Sorptomatic 1990 CE instrument. SEM was used to determine the particle morphology using a Philips XL series SEM/EDX XL 30 ESEM. Bright field TEM studies, using a Philips CM30/Super TWIN electron microscope, were conducted for the estimation of the size of the primary crystallites and nature and extent of aggregation. The BaTi₄O₉ powders were cold pressed in the form of 12 mm diameter and 2–3 mm cylindrical pellets at a compaction pressure of 250 MPa with stearic acid used as lubricant. The green pellets were sintered in static air at 1200 °C for different times to obtain highly sintered materials. The sintered densities were determined using Archimedes principle.

Results and discussion

Citric acid has three carboxylic and one hydroxy group for coordinating to metal ions and therefore prevent precipitation

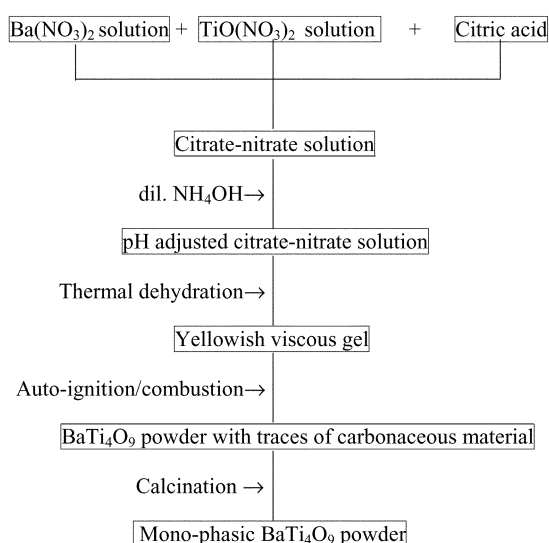


Fig. 1 Flowchart for the preparation of BaTi₄O₉ powder.

or phase separation so providing intimate blending among constituent ions.¹¹ It is a low cost material and can be combusted with nitrates (*i.e.* oxidant) at low ignition temperature (200–250 °C), and hence is a good choice as a fuel in the combustion technique.¹⁰ Tsay and Fang¹¹ observed the precipitate of barium citrate and barium titanate citrate with an excess of citric acid. On other hand Kumar *et al.*^{12,13} succeeded in obtaining viscous gels with a lower amount of citric acid probably due to involvement of nitrate ions in the gel formation.¹⁴ Barium nitrate also has a low solubility in water but Lee *et al.*¹⁵ circumvented this problem by pH adjustment as guided by a theoretical model. Titanium (due to its high ionic potential) also has a tendency to be hydrolyzed in aqueous medium, even at room temperature, if not bound by a suitable complexing agent. Our preliminary aim was to obtain viscous gels to provide atomistic level blending among constituent ions. The process parameters were fixed based on experimental observations.

The thermal dehydration of pH unadjusted citrate–nitrate solutions containing total metal ions to citric acid molar ratio even up to 1:2 resulted in precipitation. On the other hand, no precipitation or phase separation was observed when a total metal ions to citric acid molar ratio of 1:0.5 was used at pH ≈ 6. The thermal dehydration of citrate–nitrate solutions (with or without pH adjustment) with different amounts of fuel content was carried out to observe phase separation or gel formation. The observations are summarized in the Table 1.

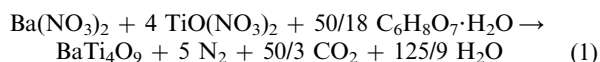
Choy *et al.*³ showed that barium and titanium complexes are most stable with citric acid at pH ≈ 6. Therefore, this value was chosen for the citrate–nitrate solutions to prevent any possibility of phase separation during the gel formation; in addition more nitrates are available at this pH for combustion with citrates. Taroaka *et al.*¹⁶ showed that dilute ammonia not only aids in dissociation of citric acid to provide more coordination sites for metal ions but also improves the solubility of the metal ions. In general, the fuel-to-oxidant ratio used in the combustion technique is defined as stoichiometric (*i.e.*, based on the concept of propellant chemistry), fuel-rich or fuel-deficient redox systems.¹⁰ However, to best of our knowledge, there are no reports available regarding the role of ammonia (which is used to adjust the pH for improving the complexation and gel formation) in combustion reactions. Therefore, in this case, generally the amount of the fuel is defined as total metal ions to complexing agent molar ratio.^{8,15,16} In combustion reactions N₂, CO₂ and H₂O are primarily evolved as gaseous products. Therefore, carbon and hydrogen are considered as reducing elements (with corresponding oxidation states of 4+ and 1+) whereas oxygen is considered as an oxidizing element with valency 2- and nitrogen is assumed to have an oxidation state of zero. Barium and titanium are considered as reducing elements with oxidation states of 2+ and 4+. Considering these valencies (oxidation states) of the individual elements, the total oxidizing valency of both barium nitrate and titanium oxynitrate is 10+ whereas the total reducing valency of citric acid is 18+.

Hence, according to the concept of propellant chemistry,¹⁷ if

Table 1 Role of the amount of citric acid and pH of the starting solution in the formation of gels

Total metal ions : citric acid molar ratio	Observations during thermal dehydration	Surface area/m ² g ⁻¹
1 : 0.25 (pH ≈ 6)	Precipitation or phase separation	—
1 : 0.50 (pH ≈ 6)	No phase separation, viscous yellowish gel	190
1 : 1 (pH ≈ 6)	No phase separation, viscous yellowish gel	115
1 : 2 (without pH adjustment)	Precipitation or phase separation	—

it is assumed that the ammonia used in the process only facilitates the gel formation and does not participate in the combustion reaction, then stoichiometric redox reaction between metal nitrate, oxynitrate and citric acid to produce one mole of BaTi_4O_9 would require a total metal ions to citric acid molar ratio of 1:0.55 (or citrate-nitrate ratio of 0.277) as represented by eqn (1):



The gels containing total metal ions to citric acid molar ratios of 1:0.5 and 1:1 are denoted 1:0.5 and 1:1 precursors, respectively.

Fig. 2(a) shows the simultaneous TG/DTA curve of the dried 1:0.5 precursor. About 98% of the total weight loss occurs during auto-ignition at about 225 °C in a very narrow temperature range and a white voluminous powder with a slight blackish tinge is obtained. The small amount of the leftover carbonaceous material is probably due to the short time available for auto-ignition (≈ 5 seconds). The XRD pattern of the powder obtained after auto-ignition of the 1:0.5 precursor (Fig. 3) shows the characteristic peaks of well-crystalline BaTi_4O_9 . The crystallite size calculated from X-ray line broadening of the (121) peak using the standard Scherrer formula was found to be ≈ 33 nm. The unit cell parameters determined using a least-squares refinement program were as follows: $a = 6.276(7)$, $b = 14.532(9)$, $c = 3.787(6)$ Å. These unit cell parameters are in good agreement with those reported in the literature.¹⁸ For a total metal ions to citric acid molar ratio of 1:1, a grayish-black dry powder was obtained after auto-ignition of the precursor. Fig. 2(b) shows the simultaneous TG/DTA curve of the dried 1:1 precursor. It was noted that only about 68% of the total weight is lost during the auto-ignition in this case and hence the powder obtained after auto-ignition contains a high amount of carbonaceous residue and the XRD pattern reflected the amorphous nature of this powder. The product obtained by calcination of the powder obtained by auto-ignition of the 1:1 precursor at 600 °C was also amorphous. Monophasic BaTi_4O_9 could be obtained only

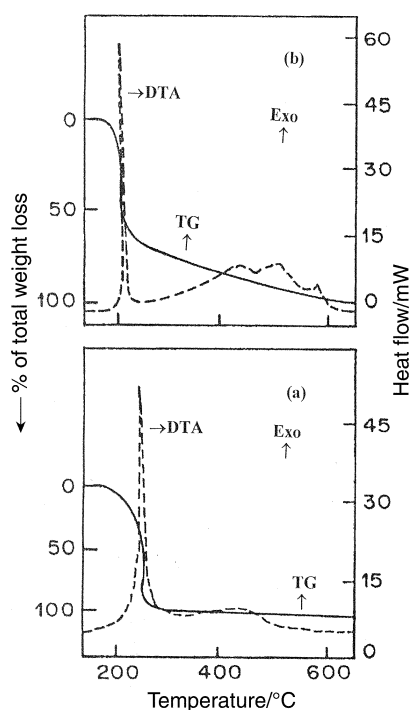


Fig. 2 Simultaneous TG/DTA curves of (a) 1:0.5 and (b) 1:1 precursors.

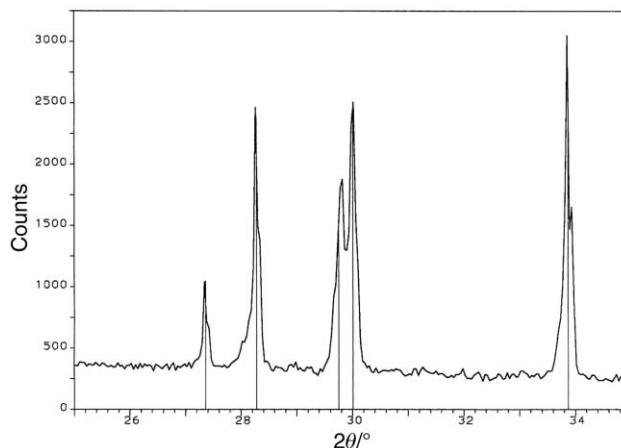


Fig. 3 XRD pattern of the uncalcined powder obtained after auto-ignition of a 1:0.5 precursor.

after calcination at 800 °C for 2 hours (XRD pattern similar to that shown in Fig. 3). The higher calcination temperature in the case of the precursor containing a higher amount of fuel to obtain monophasic BaTi_4O_9 is probably due to the higher amount of the leftover carbonaceous material after auto-ignition and multi-step decomposition of the precursor. The higher amount of the fuel may also act as a barrier in combining one mol of BaO with four mol of TiO_2 to produce BaTi_4O_9 . The simultaneous TG/DTA curves of 1:0.5 and 1:1 precursors show that there is no weight loss beyond 600 °C and therefore the residual carbonaceous material can be removed at this temperature. The major differences between our work and that of Choy *et al.*³ is that they used TiCl_4 instead of $\text{TiO}(\text{NO}_3)_2$ and also the exact amount of citric acid used for preparation of the gel was not quoted. In addition, they also obtained other barium polytitanates *i.e.*, $\text{BaTi}_5\text{O}_{11}$ and $\text{Ba}_2\text{Ti}_9\text{O}_{20}$ as intermediates as opposed to the direct synthesis of BaTi_4O_9 in the present study.

Fig. 4(a) and (b) show low magnification SEM micrographs of the BaTi_4O_9 powders obtained from 1:0.5 and 1:1 precursors, respectively. These micrographs reflect agglomerated, porous, flaky morphologies for the samples. The flame temperature is responsible for agglomeration or fused structures whereas the evolution of the large amount of gaseous products during combustion leaves highly porous voluminous powders. BaTi_4O_9 powder obtained from the 1:0.5 precursor is more porous compared to that from the 1:1 precursor. The higher porosity in case of 1:0.5 precursor is due to an almost single step decomposition during auto-ignition in this case, which allows better heat dissipation through the rapid evolution of the large volume of the gaseous products in a short time. Thus the possibility for forming a dense structure due to local lower temperature regions is minimized. The difference of the extent of porosity between 1:0.5 and 1:1 precursors is further supported by surface area and pore size distribution analyses also. The specific surface area of BaTi_4O_9 powder obtained from the 1:0.5 precursor was found to be about $190 \text{ m}^2 \text{ g}^{-1}$ whereas the 1:1 precursor resulted in a powder with the specific surface area of about $115 \text{ m}^2 \text{ g}^{-1}$. Taroaka *et al.*¹⁶ also obtained very high surface area powders prepared through pH adjusted precursors. The higher surface area in the case of the 1:0.5 precursor is again due to a rapid evolution of the large volume of the gases during auto-ignition in a short time. For the precursor containing a higher amount of the fuel, the combustion rate of citrates decreases; as a result the combusted ash is more coarse primarily due to poor heat dissipation by the evolved gases. The specific pore volumes (at $P/P_0 = 0.989$) for the BaTi_4O_9 powder, for the 1:0.5 and 1:1 precursors, were found to be *ca.* 0.1258 and $0.0527 \text{ cm}^3 \text{ g}^{-1}$, respectively, which again indicates a more porous network for

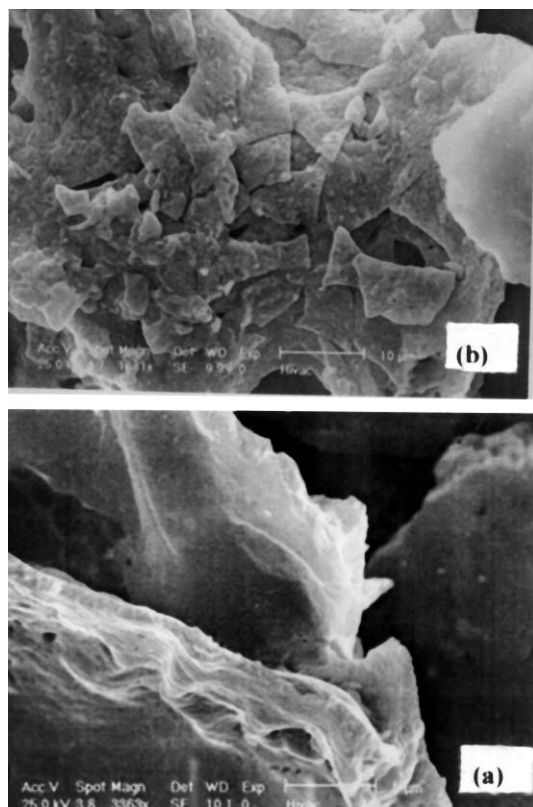


Fig. 4 SEM micrographs of BaTi_4O_9 powders prepared through (a) 1:0.5 and (b) 1:1 precursors.

the 1:0.5 precursor. Segadaes and coworkers¹⁷ showed an increase in the flame temperature with increase in the urea content which was used as a fuel during the synthesis of a ZnO based varistor powder. Roy and coworkers¹⁰ also showed the formation of hard agglomerates and reduction in surface area of Y_2O_3 powder in case of fuel-rich precursors. It was shown^{7,10} that the single step decomposition of the fuel-deficient precursor during the combustion results in a powder with high surface area and without hard agglomerates.

Fig. 5(a) and (b) show representative bright field TEM micrographs of BaTi_4O_9 powders obtained from the 1:0.5 and 1:1 precursors, respectively. Bright field TEM micrographs of the BaTi_4O_9 powder obtained from the 1:0.5 precursor showed that the primary crystallites were < 50 nm in size and had nearly round shapes. The crystallite size data obtained through TEM and X-ray line broadening are thus in good agreement. However, the 1:1 precursor led to a crystallite size of the order of ≈ 50 – 300 nm with irregular shapes. The probable reason for the formation of nearly round crystallites in the case of the 1:0.5 precursor is the single mechanism occurring during combustion *via* single step decomposition of the precursor whereas for the 1:1 precursor different reaction mechanisms are likely to occur during combustion *via* multi-step decomposition of the precursor. The reason for an increase in crystallite size in the case of the fuel-rich precursor is primarily due to the fact that combustion of a higher amount of the fuel generates more enthalpy and increases the flame temperature, which assists crystal growth. Purohit *et al.*⁷ and Ye *et al.*¹⁹ also observed an increase of crystallite size as the amount of fuel was increased due to an increase in flame temperature.

The comparative study of the powder characteristics obtained from 1:0.5 and 1:1 precursors indicates that the BaTi_4O_9 powder obtained from the 1:0.5 precursor is more suitable for sintering. Hence, sintering was performed only for this powder. The green density of the cold pressed BaTi_4O_9 powder was found to be ≈ 53 % of its theoretical density (4.522 g cm^{-3}). Green pellets of BaTi_4O_9 powder (when sintered

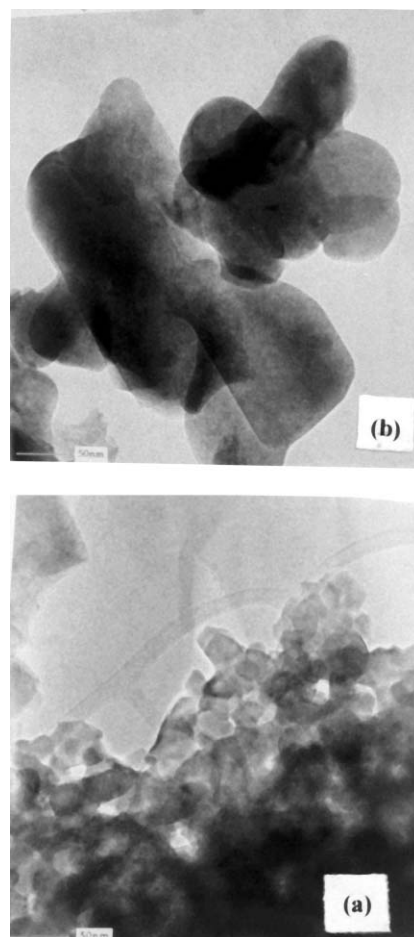


Fig. 5 Bright-field TEM micrographs of BaTi_4O_9 powders prepared from (a) 1:0.5 and (b) 1:1 precursors.

in air at 1200°C for 3 hours reached ≈ 94 % of its theoretical density whereas an increase in the sintering time to 6 hours at the same temperature resulted in ≈ 96 % of its theoretical density. The high surface area and narrow size distribution of the starting nanocrystallites are responsible for obtaining highly sintered pellets at fairly low sintering temperatures. Choy *et al.*³ also observed the importance of sintering time to obtain highly sintered BaTi_4O_9 and reported a bulk density ≈ 96 % of its theoretical density at a sintering temperature of 1200°C for 10 hours. The XRD pattern of the sintered product showed monophasic BaTi_4O_9 . Since dielectric characteristics are sensitive to the phase purity and porosity of the sintered product, BaTi_4O_9 produced through the auto-ignition route should show improved dielectric characteristics.

Conclusion

A simple wet chemical process based on the auto-ignition of gels has been developed. By controlling the process parameters, the technique has an immense potential for producing well sinterable nanocrystalline BaTi_4O_9 powder at a relatively low calcination temperature.

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