Synthesis of monophasic $Ba_2Ti_9O_{20}$ through gel combustion

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Monophasic $Ba_2Ti_9O_{20}$ has been prepared using the powder derived through an auto-ignition route. The process involves the formation of a viscous gel by thermal dehydration of the pH adjusted citrate–nitrate solution. The process parameters, for example, the amount of citric acid used for gelation and pH of the starting solution were optimized experimentally to get a stable gel with a desired decomposition behavior and favorable powder characteristics. The auto-ignition (at an external temperature of ≈ 225 °C) of the gel resulted in a voluminous, nanocrystalline (<50 nm) powder containing intimate blending of $BaTi_4O_9$ and TiO_2 with traces of carbonaceous material. The monophasic $Ba_2Ti_9O_{20}$ could be obtained at a calcination temperature of 1200 °C. The powder obtained after auto-ignition, when calcined at 600 °C and sintered at 1250 °C for 6 hours, produced $\approx 96\%$ dense, phase pure $Ba_2Ti_9O_{20}$.

Introduction

The advancement of microwave and communication technology in the past decade is apparent by an increasing number of cellular phone users. The revolution in this technology has been achieved by using the low loss and temperature stable dielectric resonators (DRs) capable of creating, selecting and filtering the microwave frequencies in the oscillators, amplifiers and tuners.[1] $Ba_2Ti_9O_{20}$ is one such low loss (quality factor $>10\,000$), temperature stable dielectric material with a reasonably high relative permittivity (≈ 39). It shows a very small change in resonant frequency as a function of temperature (≈ 4 ppm K^{-1}). Therefore, it is well suited as a dielectric resonator for use in the microwave communication technology.[2] The fabrication of very dense bodies of this material with phase purity is of great practical importance for improvement of the dielectric characteristics. However, there are only a few reports available on the low temperature synthesis of monophasic $Ba_2Ti_9O_{20}$. Choy *et al.*[3] successfully prepared the monophasic $Ba_2Ti_9O_{20}$ powder by pyrolysis of the amorphous citrate gel at 1300 °C for 2 hours. Lin *et al.*[4] could not obtain monophasic $Ba_2Ti_9O_{20}$ by a solid state reaction between $BaCO_3$ and TiO_2 even at 1360 °C for 5 hours. However, a near monophasic $Ba_2Ti_9O_{20}$ was obtained[5] by a rapid thermal processing of $BaTiO_3$ and TiO_2 at 1390 °C. The solid state synthesis has several inherent disadvantages *viz.* contamination from the grinding media and formation of unwanted phases is more common during the fabrication of the complex mixed oxide phases such as barium polytitanates. Solution chemistry routes like co-precipitation, sol–gel or combustion provide an intimate blending of the constituents in the synthesis of these materials. Therefore, the phase pure materials with improved powder characteristics, for example, narrow particle size distribution among the nano-crystallites, higher surface area and better sinterability can be obtained at a much lower calcination temperature. These processes are of further significance for electro-ceramics like barium titanates where the dielectric characteristics are highly sensitive to the impurity phases and porosity in the sintered products.

Among the available solution chemistry routes, the combustion technique is capable of producing the nanocrystalline powders of the oxide ceramics at a lower calcination temperature in a surprisingly shorter time.[6–8] The combustion technique involves an exothermic decomposition of a fuel-oxidant precursor and results in either the finely divided powder with required phase or semi-decomposed precursor with a considerable carbonaceous residue, depending upon the nature of fuel and the fuel-to-oxidant ratio used in the process.[8]

The formation of the viscous liquid or gel is a primary condition for an intimate blending of the starting constituents, and thereby preventing an inhomogeneous and incomplete redox reaction between a fuel and an oxidizer. The nature of the fuel, its amount, and pH of the starting solution are some of the important process parameters for obtaining a transparent viscous gel while avoiding any phase separation or precipitation.[9,10] The powder characteristics obtained by the combustion technique are primarily dependent on the enthalpy or the flame temperature generated during the combustion, which in turn is a function of the nature of the fuel and fuel-to-oxidant ratio used in the process.[11] The single step decomposition of the precursor during auto-ignition allows improved cooling of the resultant powder product through a rapid evolution of the gases, and this facilitates the generation of the product with high surface area and also free from hard agglomerates.

In this paper, the fabrication of a well sintered, monophasic $Ba_2Ti_9O_{20}$ using the auto-ignition route derived nanocrystalline powder is reported. The powders and sintered products obtained were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and sinterability.

Experimental

High purity $TiO(NO_3)_2$, $Ba(NO_3)_2$, citric acid ($C_6H_8O_7 \cdot H_2O$) and NH_4OH were used as the starting materials. $TiO(NO_3)_2$ was prepared by precipitation of $TiCl_4$ as hydrated titania using NH_4OH and dissolving the precipitate in a minimum volume of 1.4 M HNO_3 after complete washing of the chloride ions. $TiO(NO_3)_2$ solution was analyzed gravimetrically as TiO_2 and was shown to contain about 0.16 mol l^{-1} of titania.
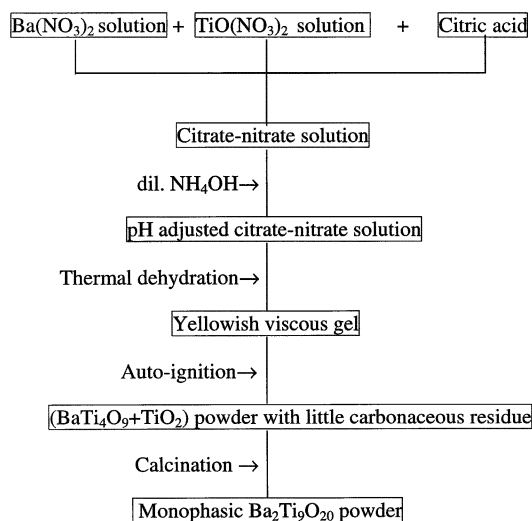
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Fig. 1 Flow chart for the synthesis of monophasic $Ba_2Ti_9O_{20}$.

$Ba(NO_3)_2$ was dissolved in hot water and cooled to room temperature. The required volume of $TiO(NO_3)_2$ solution was mixed into $Ba(NO_3)_2$ solution maintaining the Ba to Ti molar ratio as 1 : 4.5. The citric acid crystals were dissolved in this solution while maintaining the total metal ions to citric acid molar ratio as 1 : 0.5, which resulted in a transparent aqueous solution, hereafter named as citrate–nitrate solution. Dilute NH_4OH was slowly added into the citrate–nitrate solution to adjust the pH to ≈ 6. The thermal dehydration of the pH adjusted citrate–nitrate solution on a hot plate at ≈ 80 °C resulted in a highly viscous yellowish gel, hereafter named as the precursor. As soon as this gel was formed, the temperature of the hot plate was raised to ≈ 225 °C. The gel at this temperature swelled and got ignited with an evolution of a large volume of gaseous products. The auto-ignition, which remained for ≈ 5 seconds, resulted in a voluminous powder with a blackish tinge. This powder was calcined at 600 °C for 2 hours to remove the leftover carbonaceous residue, prior to the sintering. The flow chart for the synthesis of $Ba_2Ti_9O_{20}$ is given in Fig. 1. The effect of the amount of citric acid and pH of the starting citrate–nitrate solution on the gel formation has been visually observed and summarized in Table 1.

Simultaneous TG/DTA was performed on part of the dried gel precursors in a flowing air atmosphere, with a heating rate of 10 °C min^{-1}, using a SETARAM simultaneous TG/DTA instrument, Model 92-16.18 to observe the decomposition behavior and to know the minimum calcination temperature. X-Ray diffraction studies were carried out for the phase evolution of the powders obtained after auto-ignition and calcination at different temperatures. The patterns were reported from $2\theta = 25$ to $35°$, *i.e.*, the range in which most of the prominent peaks of $Ba_2Ti_9O_{20}$ are reported, with the scan rate of 1° min^{-1}, using Cu-Kα radiation on a Philips X-ray diffractometer, Model PW 1927. Bright field TEM was used for the estimation of size of the primary crystallites, and to determine the nature and extent of aggregation using a Philips CM30/Super TWIN electron microscope. The calcined powders were cold pressed in the form of 12 mm diameter and 2–3 mm height cylindrical pellets at a compaction pressure of 250 MPa. Stearic acid was used as a lubricant. The green pellets were sintered in static air at 1200 °C and 1250 °C for 6 hours to obtain the highly sintered bodies of this material. The sintered densities were determined using the Archmede's principle.

Results and discussion

Citric acid has three carboxylic and one hydroxy group for coordinating to metal ions, and therefore prevents the precipitation or phase separation and provides an intimate blending among the constituent ions.[12] It is a low cost material and can be combusted with nitrates at a low ignition temperature (200–250 °C) and it therefore provides a good choice as a fuel in the combustion technique.[11] However, Tsay *et al.*[12] observed a precipitate of barium citrate and barium titanyl citrate with an excess of citric acid. On the other hand Kumar *et al.*[13,14] obtained a viscous gel by using less citric acid, which renders more nitrates freely available for the gel formation.[15] Barium nitrate has a low solubility in water but Lee *et al.*[16] 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 an aqueous media, even at ambient temperature, if not bound by a suitable complexing agent. Our preliminary aim was to obtain a viscous gel to provide an atomistic level of blending among the constituent ions.

Choy *et al.*[3] showed that the barium and titanium complexes with citric acid are most stable at pH ≈ 6. Therefore, the pH ≈ 6 for citrate–nitrate solution was chosen to prevent any possibility of phase separation during the gel formation, and in addition at this pH more nitrates are available for combustion with citrates. Teraoka *et al.*[17] showed that dilute NH_4OH not only helps in dissociation of citric acid to provide more coordination sites for metal ions but it also improves the solubility of the metal nitrates. The observations shown in Table 1 are in agreement with those observed in the case of $BaTi_4O_9$[18] synthesized through the same auto-ignition technique. In general, the fuel-to-oxidant ratio used in the combustion technique is defined as stoichiometric or fuel-rich or fuel-deficient redox systems.[11] The net oxidizing valency of both barium nitrate and titanium oxynitrate is $10-$ whereas the net reducing valency of citric acid is $18+$, as described earlier.[18] Therefore, according to the concept of propellant chemistry, the stoichiometric redox reaction between barium nitrate, titanium oxynitrate and citric acid to produce one mole of $Ba_2Ti_9O_{20}$ would require total metal ions to citric acid molar ratio of about 1 : 0.55, as shown in the following equation:

$$2\ Ba(NO_3)_{2(c)} + 9\ TiO(NO_3)_{2(c)} + 55/9\ C_6H_8O_7 \cdot H_2O_{(c)} \rightarrow$$
$$Ba_2Ti_9O_{20(c)} + 11\ N_{2(g)} + 110/3\ CO_{2(g)} + 275/9\ H_2O_{(g)}$$

The gels containing total metal ions to citric acid molar ratio of 1 : 0.5 and 1 : 1 will be hereafter termed as 1 : 0.5 and 1 : 1 precursors, respectively. Even though gel formation is possible for both 1 : 0.5 and 1 : 1 precursors, it has previously been shown that for $BaTi_4O_9$ synthesis through the same auto-ignition technique,[18] the powder derived from the 1 : 0.5 precursor resulted in better powder characteristics. Therefore, in the present investigation the powder characteristics for only the powder derived through 1 : 0.5 precursor will be discussed. Fig. 2 shows the simultaneous TG/DTA curve of the dried 1 : 0.5 precursor and this shows a near single step exothermic decomposition at ≈ 225 °C. More than 97% of the total weight loss occurred during the auto-ignition and resulted in a white

Table 1 Effect of the amount of citric acid and pH of the starting solution on the formation of gels
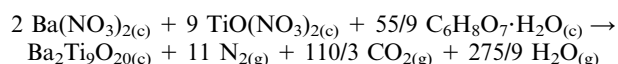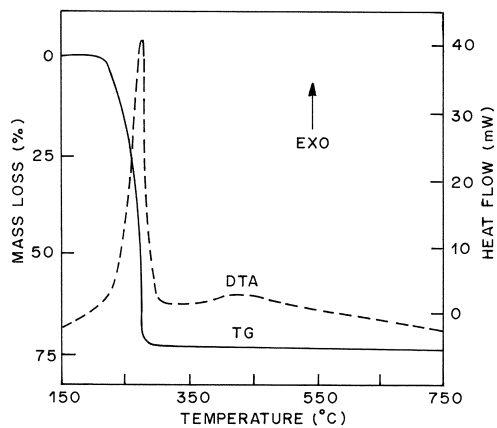
Total metal ions to citric acid molar ratio	Observations during thermal-dehydration
1 : 0.25 (pH ≈ 6)	Precipitation or phase separation
1 : 0.50 (pH ≈ 6)	No phase separation, viscous yellowish gel
1 : 1 (pH ≈ 6)	No phase separation, viscous yellowish gel
1 : 2 (without pH adjustment)	Precipitation or phase separation

Fig. 2 Simultaneous TG/DTA curve of 1 : 0.5 precursor.

Fig. 4 XRD pattern of (a) uncalcined powder (b) powder calcined at 1100 °C and (c) sintered product.

voluminous powder with a small amount of carbonaceous material. The leftover carbonaceous material is probably due to the short time available for the auto-ignition (≈ 5 seconds). The single step decomposition during an auto-ignition allows better heat dissipation through the rapid evolution of a large volume of gaseous products in a short time. Thus, the possibility of forming a dense structure in the resultant powder due to local temperature is minimized as reflected in the TEM micrograph (Fig. 3). The phase evolution from the powder obtained after the auto-ignition has been studied as a function of calcination temperature, as shown in Fig. 4. XRD pattern of the powder obtained after auto-ignition of 1 : 0.5 precursor (Fig. 4a) shows the characteristic peaks of $BaTi_4O_9$ and the most intense peak of TiO_2 (anatase). The powder obtained after calcination at 600 °C, to remove the small amount of the residual carbonaceous material, also showed a similar kind of XRD pattern. Since, the crystallite size (Fig. 3) obtained for this powder is very fine (<50 nm, with most of the crystallites around 10 nm), this gives rise to the formation of higher temperature phase of TiO_2 at room temperature. This observation is in agreement with Ayllon et al.[19] and Kluson et al.[20] who also obtained the anatase phase at room temperature for mesoporous, nanocrystalline TiO_2 powder, which was attributed to particle size induced phase stabilization. Therefore, the powder obtained after auto-ignition appears to have an intimate blending of $BaTi_4O_9$ and TiO_2. It may be noted that the direct synthesis of the desired $Ba_2Ti_9O_{20}$ phase could not be achieved unlike $BaTi_4O_9$ through the same auto-ignition technique, as reported earlier.[18] This may be due to the existence of flame temperature for a very short time (≈ 5 seconds), which appears to be insufficient for the synthesis of $Ba_2Ti_9O_{20}$. The characteristics peaks of $Ba_2Ti_9O_{20}$ started to
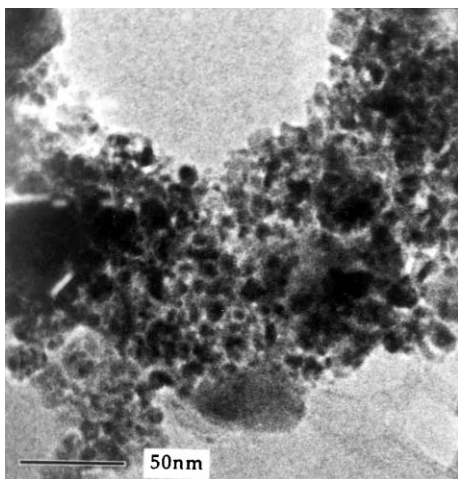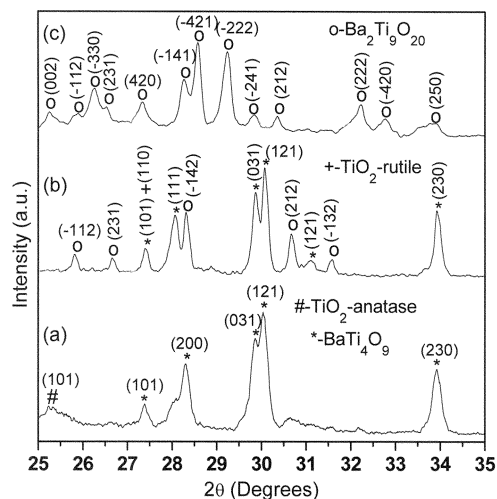
appear at 900 °C and their intensity increased as a function of calcination temperature with a concomitant reduction of $BaTi_4O_9$ phase. Fig. 4 (b) shows the XRD pattern of the powder calcined at 1100 °C for 2 hours, which correspond to a mixture of $BaTi_4O_9$, $Ba_2Ti_9O_{20}$ and TiO_2 (rutile).

The transformation of anatase to rutile is attributed to an increase in particle size and higher temperature. Kluson et al.[20] also observed the conversion of anatase $\rightarrow$ rutile phase on calcination at a higher temperature. The monophasic $Ba_2Ti_9O_{20}$ could be obtained at a calcination temperature of 1200 °C for 4 hours. In order to get the sintered product of $Ba_2Ti_9O_{20}$, the powder obtained after calcination at 600 °C for 2 hours was cold pressed and sintered. During the sintering required phase formation also takes place. Fig. 4c shows the XRD pattern of the pellet sintered at 1200 °C for 6 hours. All the peaks corresponded to monophasic $Ba_2Ti_9O_{20}$. The intimate blending of the nanocrystalline $BaTi_4O_9$ and TiO_2 (Fig. 3) in the starting powder used for sintering facilitates the formation of the $Ba_2Ti_9O_{20}$ phase. Fig. 5 shows bright field TEM micrographs of the powder calcined at 1100 °C, and this shows the particle morphology and primary crystallite size just before the phase formation and sintering. The TEM micrograph shows the primary crystallite size ranging from ≈ 50 nm to ≈ 300 nm, which should facilitate a better sintering.

The calcined powder used for sintering contains intimate blending of $BaTi_4O_9$ ($\rho_{th} = 4.522$ g cm^{-3}) and TiO_2-anatase ($\rho_{th} = 3.904$ g cm^{-3}) in the molar ratio of 1 : 0.5. Hence, the theoretical density of this powder is equal to $(1 \times 4.522 + 0.5 \times 3.904)/(1.50) = 4.316$ g cm^{-3}. The geometrical green density of the pellets was found to be $\approx 53\%$ of the theoretical

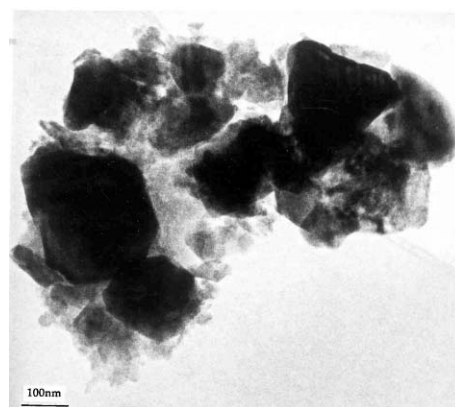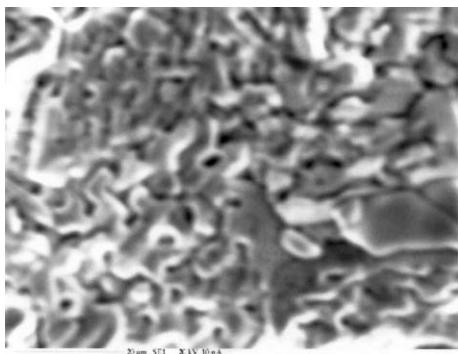Fig. 3 Bright-field TEM micrograph of the powder calcined at 600 °C.

Fig. 5 Bright-field TEM micrographs of the powder calcined at 1100 °C.

Fig. 6 Microstructure of the sintered pellet of Ba$_2$Ti$_9$O$_{20}$.

density. The calcined (at 600 °C) powder when sintered at 1200 °C for 6 hours reached ≈92% of the theoretical density (4.577 g cm^{-3}). The increase in sintering temperature to 1250 °C for 6 hours resulted in ≈96% of the theoretical density. Fig. 6 shows the SEM micrograph (secondary electron image) of the well-sintered pellet.

Conclusion

A simple wet chemical process based on the auto-ignition of the citrate–nitrate gel has been developed. The technique has an immense potential for producing intimate blending of nano-crystalline BaTi$_4$O$_9$ and TiO$_2$ powder which subsequently resulted in very dense (96%), monophasic Ba$_2$Ti$_9$O$_{20}$ at 1250 °C for 6 hours.

Acknowledgement

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