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Preparation of barium strontium titanate using a modified polymeric precursor method

K. Venkata Saravanan · K. C. James Raju ·
M. Ghanashyam Krishna · Anil K. Bhatnagar

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Abstract Barium strontium titanate with Ba/Sr ratio of 50/50 (BST5) was prepared using a modified polymeric precursor method. Unlike other methods, it proved to be cost effective since neither moisture sensitive nor costly starting materials were used for the preparation. The optimum preparation condition was established, and it was found that an annealing temperature of 600 °C with a dwell time of 20 h followed by a heat treatment at 800 °C with dwelling time of 4 h is enough to obtain well crystallized, phase pure fine powder of BST5. The oxide powder thus obtained was single phased, crystalline with cubic structure. The average lattice constant of the polycrystalline oxide was examined using XRD and it was determined to be 0.3950 nm (±0.0003 nm). The average crystallite size of the ceramic was found to be about 25–30 nm. The reaction pathway, temperature of decomposition of the precursor and the temperature of formation of the oxide was found using the data from the EGA-TGA-MS coupled instrument. TGA data showed about 75% of total weight loss over the entire heating process. The SEM studies showed that the grains were in micrometer size range, having high degree of agglomeration and irregular morphology. This process is interesting as it yields phase pure BST5 ceramic at a temperature of 800 °C devoid of secondary phases like $(Ba,Sr)_2TiO_4$.

Introduction

Perovskite type ferroelectric materials have been extensively studied in the recent past for their spectrum of applications [1–6]. Amongst various ferroelectric materials, barium titanate and related compounds have been very promising for the realization of a wide range of devices such as positive temperature coefficient (PTC) resistors [7], ferroelectric memories [8], high dielectric constant capacitors and transducers [9]. Sr-substituted $BaTiO_3$ is considered potentially a better material for a variety of electronic materials such as tunable capacitors for RF and microwave applications, oscillators, tunable microwave filters and phase shifters, integrated capacitors such as the one used in dynamic random access memories (DRAMs) and the gate insulator in the next generation of metal oxide semiconductor field effect transistors [10–14]. When Ba atoms are partially replaced by Sr atoms in a $BaTiO_3$ matrix, the phase transition temperature (Curie Temperature, T_c) from paraelectric to ferroelectric phase decreases linearly from 120 °C (for $BaTiO_3$) to –165 °C (for $SrTiO_3$). Thus the temperature range, in which the ferroelectric phase exists, can be easily controlled by adjusting the Ba/Sr ratio. Barium strontium titanate ($Ba_x,Sr_{1-x}TiO_3$) is ferroelectric at room temperature (RT) when the Ba/Sr ratio is greater than 70/30 and it is paraelectric when

K. V. Saravanan · K. C. James Raju (✉) ·
M. G. Krishna · A. K. Bhatnagar
School of Physics, University of Hyderabad,
Hyderabad 500 046, India
e-mail: kcjrsp@uohyd.ernet.in

Present Address:
A. K. Bhatnagar
Pondicherry University, R.V. Nagar, Kalapet,
Pondicherry 605 014, India

this ratio is less than 70/30. In the present study the composition of interest is $Ba_{0.5}Sr_{0.5}TiO_3$ (i.e., $x = 0.5$).

Synthesis of barium strontium titanate (BST) in bulk ceramic form has been reported using various techniques. Conventionally, various compositions of BST have been prepared by high temperature ceramic method [15] in which fine powders of $BaCO_3$, $SrCO_3$ and TiO_2 are thoroughly mixed and then heated at high temperatures (>1,200 °C). This preparation method normally yields large grain size and non-homogenous product with a high degree of porosity, which is not found good for the fabrication of high performance devices. Even though the attrition milling [16] technique yields products with smaller grain size, undesirable contamination gets incorporated in the material due to the wear of the milling balls affecting the performance of devices.

Apart from the conventional ceramic method and attrition milling technique several low temperature methods like acetate based sol gel method [17], oxalate precursor method [18], coprecipitation methods [19, 20] are found to be better alternatives. However, these methods use expensive starting materials. Pechini's method [21] based citrate precursor method [22]/polymeric precursor method [23] is considered to be cost effective because of low cost starting materials. But, they use moisture sensitive metal alkoxides, which requires careful control of inert atmosphere.

There is no method reported previously, to the best of our knowledge, which prove to be cost effective and also do not use moisture sensitive materials. In this work, BST5 has been successfully prepared by replacing moisture sensitive metal alkoxides with simple metal oxides.

We were successful in preparing BST5 employing $BaCO_3$, $SrCO_3$ and TiO_2 using a modified polymeric precursor method/citrate precursor method. DTA/TG and TG/EGA-MS [24] techniques have been employed to study the reaction pathway during thermal decomposition of the precursor. BST5, prepared by this method, has been characterized by X-ray diffraction (XRD), FT-IR and SEM studies.

Experimental procedure

Preparation of $TiO_2{\cdot}xH_2O$

$TiO_2{\cdot}xH_2O$ was prepared based on the technique reported by Das and Pramanik [25]. The required amount of TiO_2 (LOBA Chemie, 99%) was dissolved in hydrofluoric acid (HF > 7 mol). The mixture was allowed to stay until a clear solution was obtained. The solution, thus obtained, was termed as the fluoride complex. In order to precipitate the hydrous titanium oxide ($TiO_2{\cdot}xH_2O$), diluted ammonia solution was added to the fluoride complex drop by drop along the rim of the container, which was placed in a water bath. Care was taken in adjusting the pH between 6 and 7. The hydrous oxide was separated from the solution and was washed with dilute ammonia to make the precipitate free from fluoride ions.

Preparation of hydrous titanium oxide-citric acid solution

The hydrous titanium oxide, prepared above, was dissolved in citric acid (LOBA Chemie, 99.7%) solution. The molar ratio of metal/citric acid was chosen as 1/4. To ensure complete homogeneity, the mixture was refluxed at about 120 °C for 2–3 h, accompanied by vigorous mixing. The solution thus obtained was termed as the titanium citrate complex.

Preparation of barium-strontium-titanyl citrate solution

Calculated amount of carbonates of barium (LOBA Chemie, 99%) and strontium (LOBA Chemie, 99%) were dissolved in citric acid solution under stirring at about 80 °C. Thereafter, ethylene glycol (Thomas Bakers, 99.5%) was added to stabilize the solution and was allowed to stay overnight. The molar ratio of metal/citric acid/ethylene glycol was 1/4/16. To this barium-strontium citrate solution, the titanium citrate complex was added and refluxed at 120 °C with intermediate stirring until a clear transparent solution without any visible impurities was obtained. This solution was named the parent solution (or stock solution). The parent solution was kept at 180 °C for 10 h to evaporate the solvents and to promote polymerization. The solution, eventually, became a black fluffy mass, which was ground in to a fine powder in acetone medium to prevent the material loss. This was referred to as the precursor. The flow chart for the preparation of BST5 bulk is shown in Fig. 1.

In order to trace the temperature of decomposition and that of formation, Setsys 16/18 (M/S Setaram, France) TGA/DTA coupled HAL2C (M/S Hiden Analyticals, UK) Mass Spectrometer was used for the thermogravimetric/differential thermal analysis/mass spectroscopy study. FT-IR spectra were collected using a Jasco FT/IR-5300 Spectrometer in the range 4,000–400 cm^{-1}. Both the precursor and the pure ceramic powder obtained after decomposition of the precursor were mixed with KBr and pressed in to pellets to

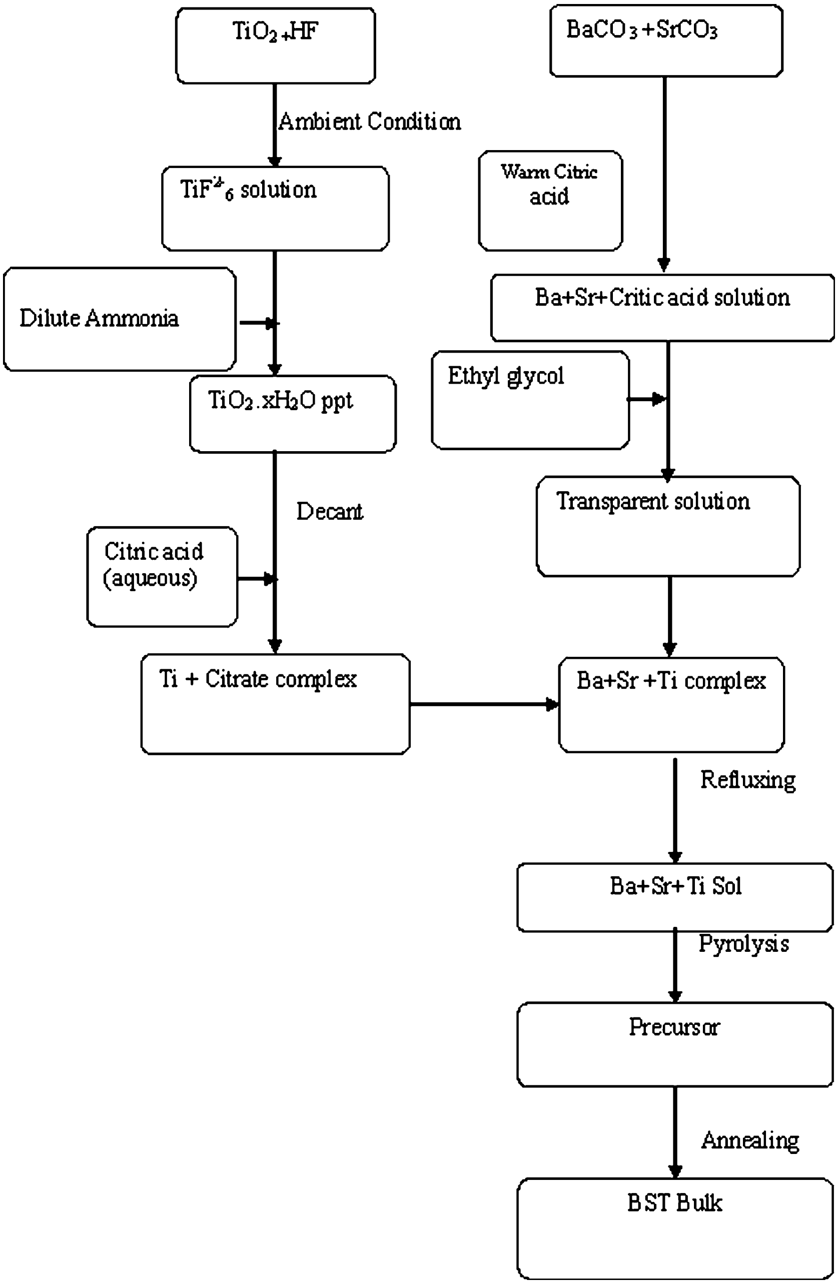


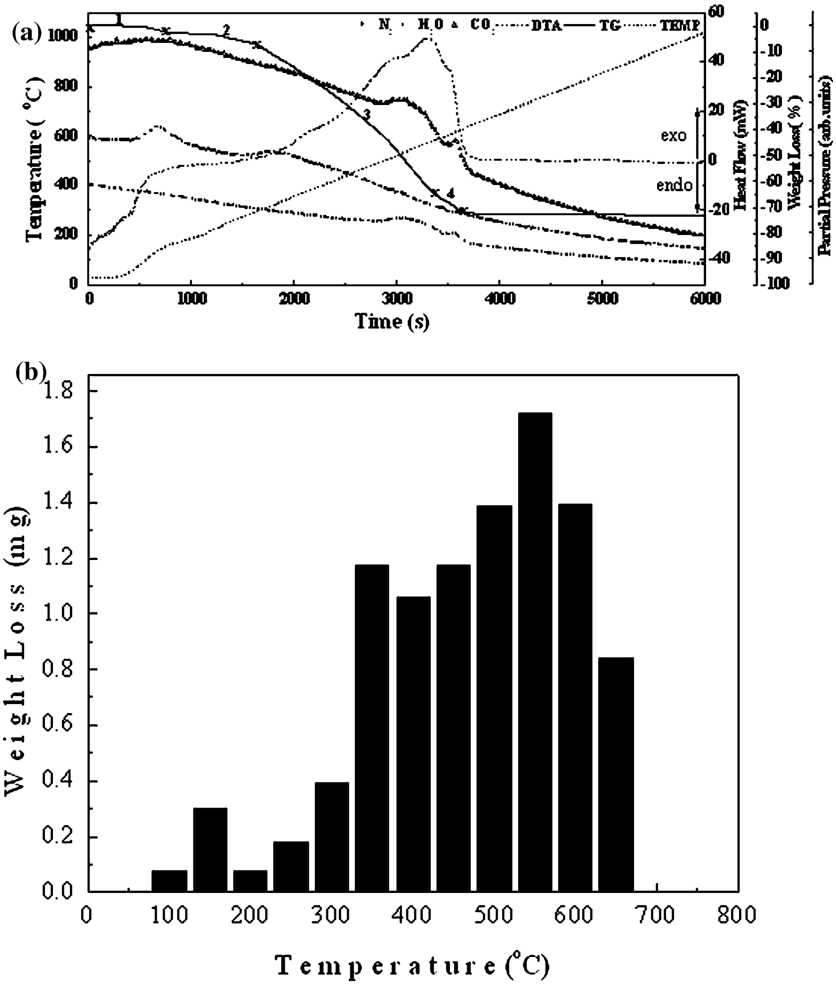
Fig. 1 Flow diagram of the synthesis of BST5 powder by modified polymeric precursor method

record the infrared spectra. The crystalline phase of BST5 ceramic at room temperature was characterized by powder X-ray diffraction using Philip PW 1830/40 X-ray diffractometer with Ni-filtered copper target (CuK_α, $\lambda = 0.1542$ nm) operated at 40 kV and 25 mA and the lattice parameters were determined. The average crystallite size was calculated using Scherrer's formula [26] ($D = 0.9\lambda/\beta \cos \theta$), where D is the crystallite size, λ the X-ray wavelength, β is the FWHM of the diffraction peak, θ the diffraction angle and K is Scherrer's constant of the order of one. A Philips XL-30 Scanning Electron Microscope was employed to ascertain grain size, shape and degree of agglomeration.

Results and discussions

The results of our thermo-analytical investigations are shown in Fig. 2. The precursor, 13.52 mg in weight, was taken in a platinum crucible for the study. The heating rate was 10 °C/min. The measurement was done from 27 to 1,000 °C in air ambient. The thermal analysis plot of the BST5 precursor is shown in Fig. 2a. Four stages

Fig. 2 (**a**) EGA-TGA-MS plots of precursor synthesized by polymeric precursor method. (**b**) Weight loss of the precursor synthesized by modified polymeric precursor method



of weight loss are observed in the TGA plot. The weight loss of the precursor as a function of increasing temperature from room temperature to 800 °C is shown in Fig. 2b. The first two stages of weight loss between 20 and 260 °C contributing ~8.5% of the total weight loss is related to the elimination of water, which corresponds to an endothermic peak of the DTA plot at 130 °C. The third stage of weight loss in the temperature range 260–580 °C is due to polycondensation, breaking away of polymeric chains formed by polyestrification, decarbonization of $BaCO_3$ and $SrCO_3$ and decomposition of other ingredients which corresponds to the DTA peaks at 300, 520 and 560 °C. About 60% of total weight loss is observed in this stage. The last stage of weight loss between 580 and 650 °C is about 5%, corresponding to the DTA peak at 610 °C, which indicates the final decomposition of the precursor and the formation of the ceramic material. No appreciable weight loss was observed after 700 °C. Similar observations have been reported earlier [23].The structural and phase characterization of the material were done by powder X-ray diffraction measurements at room temperature. Based on the EGA-TGA-MS data, the annealing temperature of the precursor was determined. The XRD patterns on different samples prepared in the present study are shown in Fig. 3. FT-IR studies were carried out after each heat treatment and the spectra of all samples are shown in Fig. 4.The XRD pattern of the as-obtained precursor without any heat treatment is shown in Fig. 3a. It is observed to be amorphous in nature. The corresponding FTIR spectrum in Fig. 4a shows that IR bands due to O–H stretch (3,600 cm^{-1}), CO_3^{2-} (1,269 cm^{-1}), carboxylate anions (1,458 cm^{-1}) and ester ions (1,735 cm^{-1}) are present along with $-C\equiv N$ (2,361 cm^{-1}), C–F (1,165 cm^{-1}) and CH_2–NH_2 (750 cm^{-1}) bands [22, 23, 27].

As the DTA data showed a broad exothermic signal at 500 °C, the precursor was heated at 500 °C, with a dwell time of 20 h. The XRD pattern of the material after this heat treatment is shown in Fig. 3b. Broad peaks at 2θ values of 25.7°, 44.56° and 52.5° are

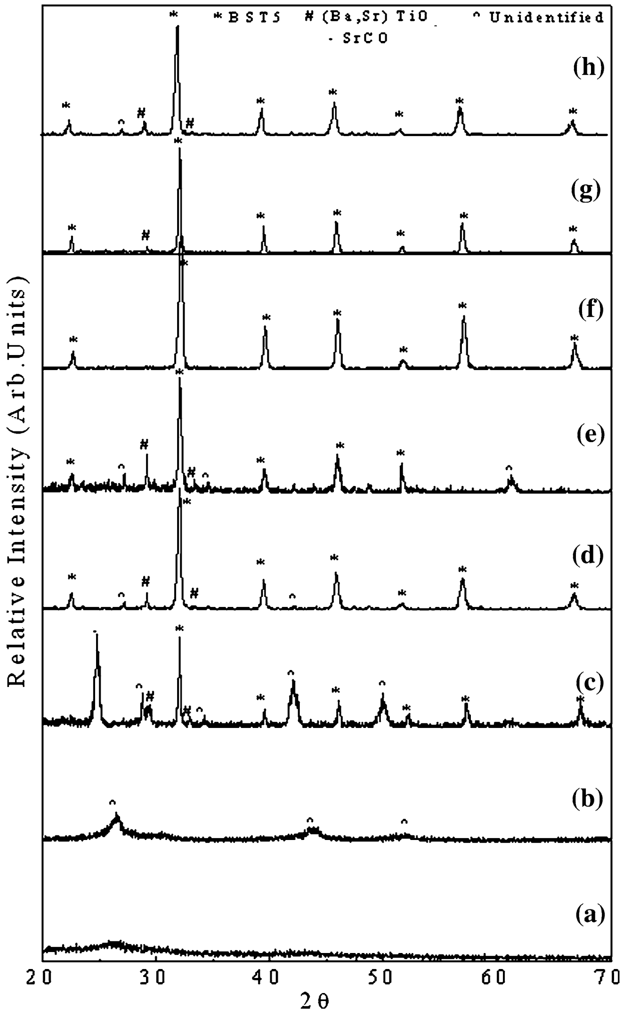


Fig. 3 X-ray diffraction pattern of the precursor after various heat treatments: (**a**) as obtained, (**b**) 500 °C for 20 h, (**c**) 600 °C for 20 h, (**d**) 800 °C for 20 h, (**e**) 500 °C for 20 h followed by 800 °C for 4 h, (**f**) 600 °C for 20 h followed by 800 °C for 4 h, (**g**) 600 °C for 20 h followed by 800 °C for 3 h, (**h**) 600 °C for 20 h followed by 750 °C for 4 h

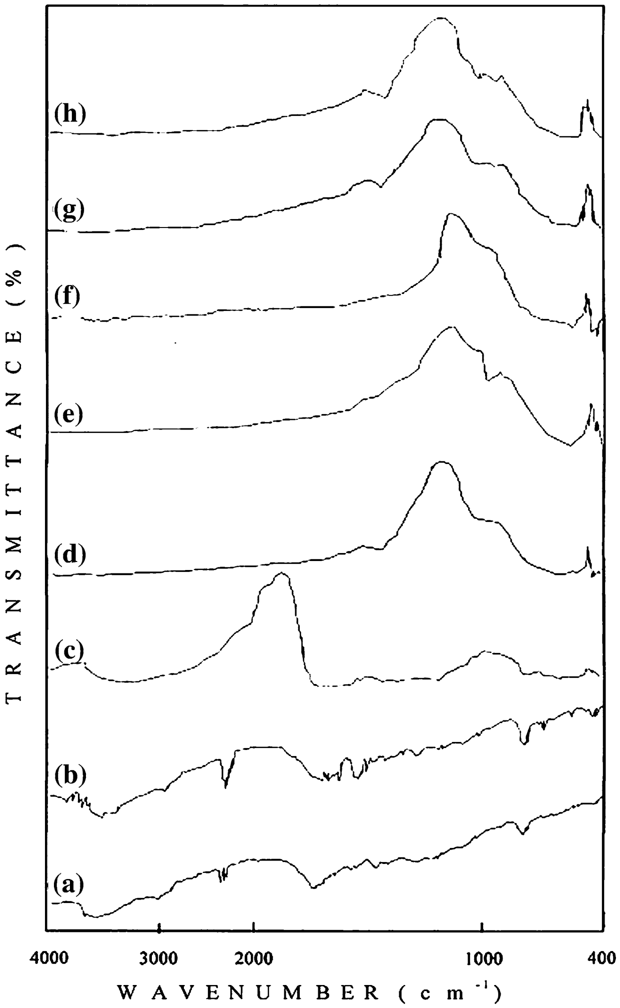


Fig. 4 FT-IR spectra of the precursor after various heat treatments: (**a**) as obtained, (**b**) 500 °C for 20 h, (**c**) 600 °C for 20 h, (**d**) 800 °C for 20 h, (**e**) 500 °C for 20 h followed by 800 °C for 4 h, (**f**) 600°C for 20 h followed by 800 °C for 4 h, (**g**) 600 °C for 20 h followed by 800 °C for 3 h, (**h**) 600 °C for 20 h followed by 750 °C for 4 h

observed, which indicate the onset of crystallization at this temperature. However, these broad peaks do not indicate the existence of the perovskite structure. Almost the same groups were present in the precursor heated at 500 °C for 20 h as shown in the IR spectrum of the unheated precursor in Fig. 4b. The presence of CH_2–NH_2, C–F, –C ≡ N may be due to the addition of HF (as solvent) and ammonia.

The precursor was heated at 600 °C for 20 h because the thermal analysis showed a narrow peak around the same temperature. It was further observed from the EGA-MS plot that, at this temperature gaseous CO_2 and N_2 evolve indicating that the decomposition gets complete at this temperature. The XRD pattern of the material, after this heat treatment, is shown in Fig. 3c. Even though the peaks corresponding to the perovskite phase seem to appear in the XRD, there are a number of other peaks, corresponding to the presence of secondary phases. This is further confirmed by the IR study as shown in Fig. 4c, which shows the IR spectrum of the same sample. Due to decomposition, the CH_2–NH_2, C–F and –C ≡ N bands present in the previous two cases disappear in this spectrum. It is evident from the EGA-MS curve that nitrogen is evolved around 540 and 600 °C. Bands corresponding to O–H, ester and CO_3^{2-} are still observed.

Even though the precursor was heated at 800 °C for 20 h, the impurity due to the secondary phases was still present as seen in the XRD of Fig. 3d. It has been reported earlier in literature that with a decomposition temperature of more than 727 °C, barium carbonate is highly stable and formed easily during the removal of organic contents [28]. The broad Ti–O band, which is normally present in $BaTiO_3$, is clearly visible (592 cm^{-1}) in the IR spectrum of the precursor heated at 800 °C for 20 h shown in Fig. 4d. It can be observed that the bands corresponding to the CO_3^{2-} have reduced in intensity.

In order to track the influence of heat treatment on the formation of phase pure BST5 powder, the precursor was subjected to two-stage heat treatment. The precursor was heated initially at 500 °C with a dwell time of 20 h and then the temperature was raised to 800 °C with a dwell time of 4 h. The XRD pattern, taken after this treatment, is shown in Fig. 3e, which reveals that the secondary phases were still dominant. The IR spectrum of this sample, in Fig. 4e showed that even though the Ti–O band [22, 23] became more intense, CO_3^{2-} seems to be still present. It was then concluded that the precursor has to be decomposed thoroughly till the perovskite phase appears.

Accordingly the precursor was heated at 600 °C for 20 h and then to 800 °C for 4 h and its XRD pattern is shown in Fig. 3f. It shows that this heat treatment yields a phase pure BST5 powder. A broad, intense Ti–O band and the disappearance of other bands in Fig. 4f is the indication of single phase BST5 ceramic material, confirming the XRD study.

In order to optimize the preparation time and temperature, the precursor was heated at 600 °C for 20 h followed by 800 °C for 3 h and 600 °C for 20 h followed 750 °C for 4 h. The XRD patterns are shown in Fig. 3g, h, respectively, and their FTIR spectra are shown in Fig. 4g, h, respectively. These spectra also do not show phase pure BST5 ceramic.

As these treatments did not yield the desired phase pure BST5 ceramic, it could be concluded that not only a two stage heating procedure but also the annealing temperature and dwelling time are important. Hence, to prepare a phase pure BST5 ceramic through this route, the precursor has to be heated at 600 °C for 20 h followed by 800 °C for 4 h. The importance of obtaining phase pure perovskite without secondary phases like $(Ba,Sr)_2TiO_4$ is indeed emphasized by previous workers such as Beck et al. [17].Scanning Electron Microscope (SEM) images were taken for phase pure ceramic samples. Grain size, shape and degree of agglomeration of the samples were observed. Figure 5a, b shows the microstructure of the pressed powder and Fig. 5c shows the microstructure of the coarse powder. From these images it is observed that the grains are in micrometer size range, with high degree of agglomeration and the grains have an irregular morphology.

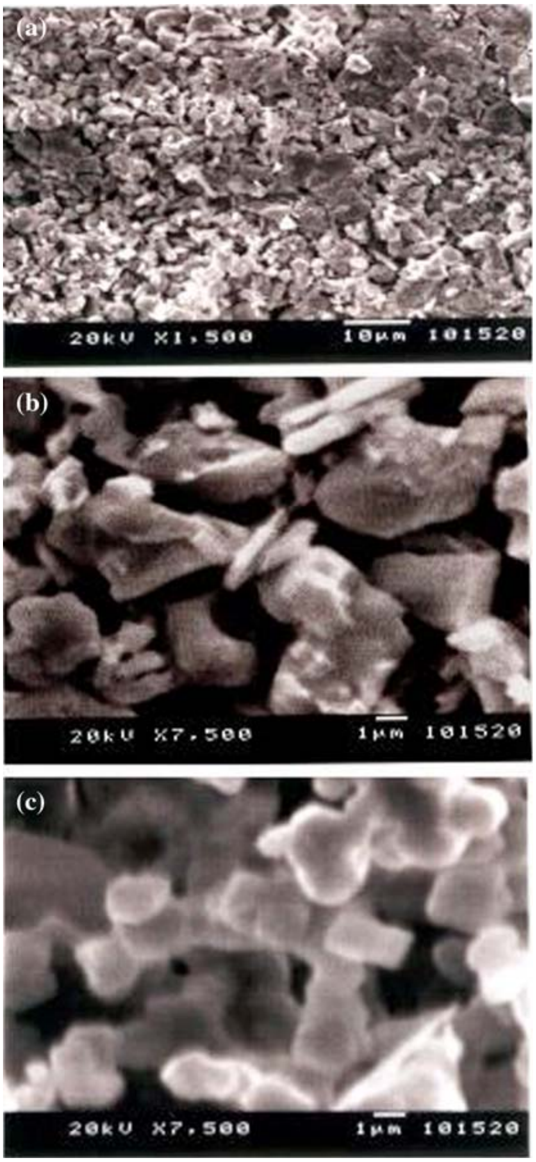


Fig. 5 (**a**, **b**) SEM photographs of pelletized $(Ba_{0.5},Sr_{0.5})TiO_3$ and (**c**) SEM photograph of powder $(Ba_{0.5},Sr_{0.5})TiO_3$

Conclusion

Barium strontium titanate powder of $(Ba_{0.5},Sr_{0.5})TiO_3$ or BST5 has been prepared using low cost, non-moisture sensitive starting materials by a modified polymeric precursor method. Homogenous BST5 powder was obtained after calcining the precursor at 600 °C for 20 h followed by 800 °C for 4 h. This process is interesting as it yields phase pure BST5 ceramic at a temperature of 800 °C devoid of secondary phases like $(Ba,Sr)_2TiO_4$. The obtained powder was characterized using XRD, FTIR and SEM. EGA-TGA-MS study was carried out in order to track the reaction pathway.

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