Engineering Sciences International Research Journal
ISSN (Print) : 2330 – 4338 ; Volume 1 Issue 1 ǁ February. 2013 ǁ

Synthesis and Charecterization of Barium Strantium Titanate Nanocrystal By Sol – Gel Method

N. Ramakoteswara Rao[1]

Abstract: Barium StrontiumTitanate (BST) was synthesized via the simple sol-gel method by using tetrabutyl titanate, ethanol, citric acid and ethylene glycol as starting material. It was heated to 130 °C for 11 h to form xerogel. The xerogel was heated at 300 °C for 2 h and subsequently it was calcined at various temperatures for 90 min.IR spectra of the xerogel were recorded with a FT-IR spectrometer (Bruker Vektor33) in the range 400–4000cm–1.Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the precursor were carried out in static air under a heating rate of 10 °C/min, from room temperature to 1000 °C. The microstructure of the BST powders was investigated by transmission electron microscopy (Philips EM208). X-ray diffraction (XRD) with CuKα radiation (Philips PW3710) was carried out to examine the phase composition of the obtained BST powder and confirmed by transition electron microscopy (TEM) for the calcination temperature of 750 ^{0}C. It was found that the particles of BST powders calcined at 750 °C were smaller, more homogeneous. Rectangle in shape and uniform than those obtained at higher temperatures.

Keywords: Barium Strontium Titanate, Nanopowder- synthesis, Nano-electroceramics, Sintering, Sol-gel.

1. INTRODUCTION

Barium strontium titanate (BST) is a useful electronic material due to its high electric permittivity and the Curie temperature depending upon the composition [1].BST is applied in piezoelectric sensors, dynamic random access memories, microwave phase shifters and uncooled infrared detectors because of its good dielectric, ferroelectric, and pyroelectric properties [2–4].High chemical purity and a uniform microstructure are the most important features for BST ceramics. Furthermore, the outstanding dielectric property observed on fine grained BST ceramics has motivated the interest in the synthesis of nanocrystalline BST. To achieve a fine microstructure and high performance, it is necessary to fabricate a fine, stoichiometric and narrow size distribution powder. For this purpose, several wet chemical non-conventional methods, such as sol-gel, self-propagating high temperature synthesis and hydrothermal techniques, were proposed as alternative approaches for the synthesis of dry mixed oxides, in order to improve the microstructural homogeneity and chemical reaction at low temperatures [5–9]. This paper presents a simple process for the synthesis of nanocrystalline BST powders.

2. EXPERIMENTAL METHOD

Materials. BST powders were synthesized by the method shown schematically in Fig 1. For the preparation of the precursor solution, barium carbonate (99.0%), strontium carbonate (98.0%), tetrabutyl titanate (98%), citric acid (99.5%), and ethylene glycol (EG) were used as starting materials. First, 0.1 mol of Ti(C4H9O)4 was dissolved into 2 moles of ethylene glycol. The mixture was stirred for about 3 min until it became transparent. Subsequently, 0.5 mol of citric acid powder and 0.1 mol water were directly added to this solution. A small quantity of white precipitate was observed at first, but immediately dissolved after stirring for 20 min with a magnetic stirrer and the solution reverted back to clear appearance. Then, the stoichiometric amounts of BaCO3 and SrCO3 powders were added to this solution. Then, the mixed solution was put into a water bath and stirred at 75 °C, until it became pale brown and transparent. Then it was heated to 130 °C for 11 h to form xerogel. The xerogel was heated at 300 °C for 2 h and subsequently it was calcined at various temperatures for 90 min.

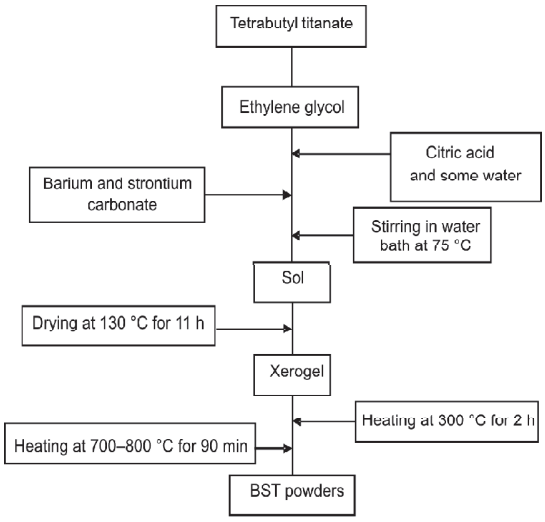

Fig. 1. Flow chart of synthesis BST nanoparticles

ISBN: 978-93-81583-90-6

Characterization. IR spectra of the xerogel were recorded with a FT-IR spectrometer (Bruker Vektor33) in the range 400–4000 cm–1. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) of the precursor were carried out in static air under a heating rate of 10 °C/min, from room temperature to 1000 °C (Shimadzu 60AH). X-ray diffraction (XRD) with CuKα radiation (Philips PW3710) was carried out to examine the phase composition of the obtained BST powders. The microstructure of the BST powders was investigated by transmission electron microscopy (Philips EM208).

3. RESULTS AND DISCUSSION

Figure 2 shows the IR spectrum of the precursor. Though it was very complex, the presence of broad bands centred at 3447 cm^{-1} (water stretching vibrations) [10], 2939 cm^{-1}(C–H stretching modes) [11], 1341 cm^{-1} (OH deformations of primary alcohols), 1065, 1955 cm^{-1} (C–O stretching vibration of primary alcohols) [11], 932 cm^{-1} (O–Ti–O stretching modes) [12] were evident. All the carbonates dissolved and thus no peaks corresponding to carbonates were found.

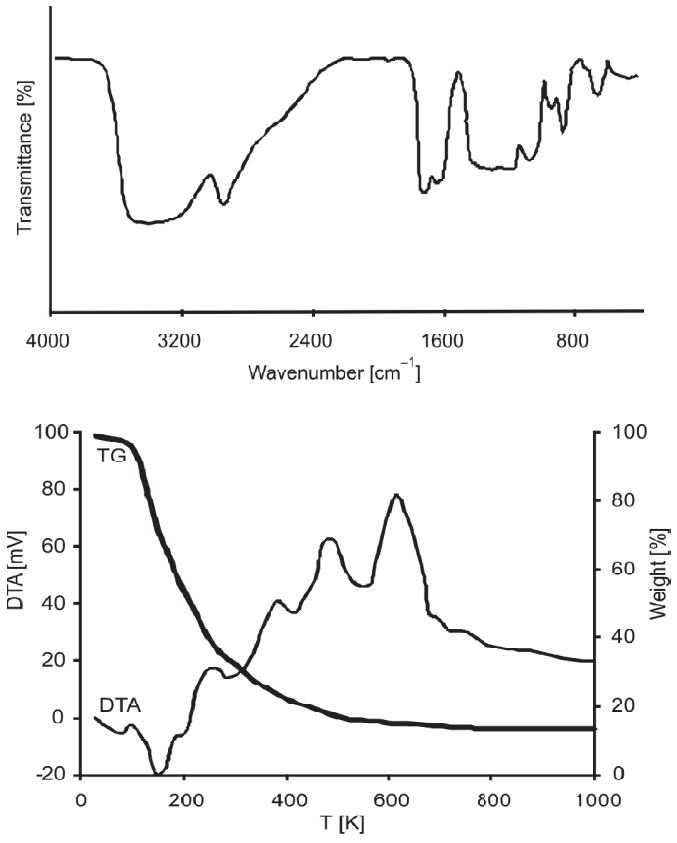

Fig. 3. TG and DTA curves of the xerogel in static air from room temperature to 1000 °C

In order to determine the temperature of synthesis BST powders, TG and DTA measurements of the xerogel were made and the results are shown in Fig.3. The TG trace indicates there were three minima in the sample weight. They occurred over the temperature ranges of 31–108, 108–630 and 630–830 ^{0}C. During the first step, the weight loss was close to 3.9%, which can be attributing to the evaporation of trapped water. An endothermic peak near 98 °C was found in the DTA curve. the second step, with the weight loss of 83.5%, was recorded for the decomposition of the citrate precursor. This process consisted of two stages, as can be deduced from the position of endothermic and exothermic peaks in the DTA curve. In the first stage from 108 to 225 °C, the endothermic peak at 155 °C was attributed to the removal of the organic parts which combined weakly with the other in the precursor. on the hand, there were three sharp exothermic peaks around 385, 475.623 ^{0}C during the second stage, which corresponded to drastic combustion of organic species involved in the precursor.

There was a small mass loss of ca. 1.5% during the last step, accompanied with an endothermic peak at 673 °C which corresponded to the decomposition of residual carbonate and is confirmed by XRD.

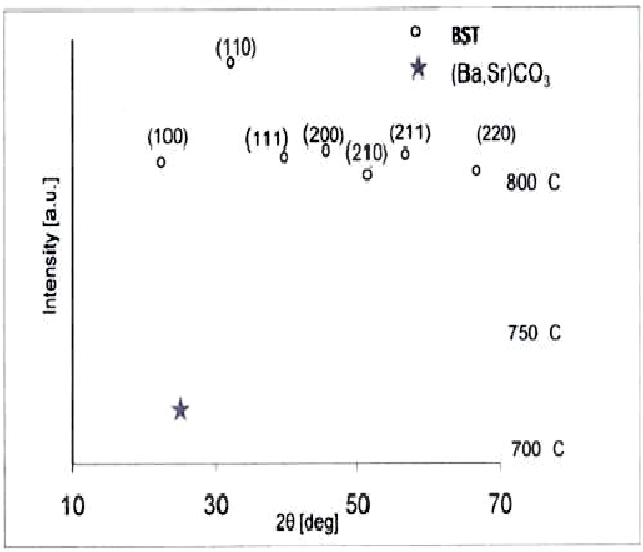

Fig. 4. XRD patterns of the BST powders synthesized at different temperatures

It can be seen that at 700 °C, weak lines occurred at 42.2^0 , corresponding to the residual carbonates phase such as BaCO3, SrCO3 and(Ba,Sr)CO3 [13]. At higher temperatures, these peaks disappeared and a pure BST phase was identified at 750 °C and 800 °C. This indicates that as the temperature increased, residual carbonates decomposed.

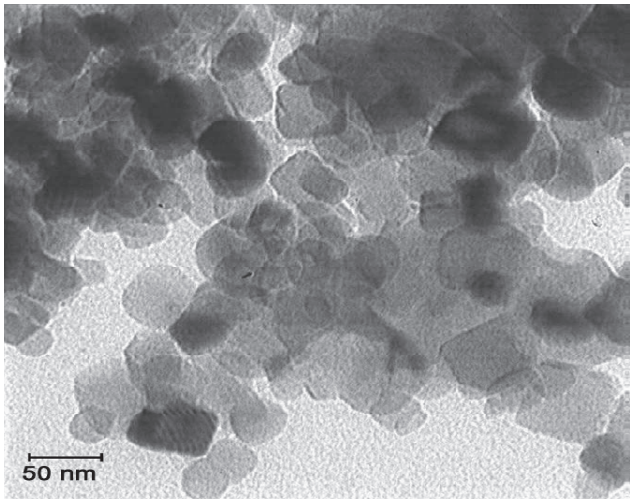

Fig. 5. Shows the TEM image of the particles obtained at 750 °C.

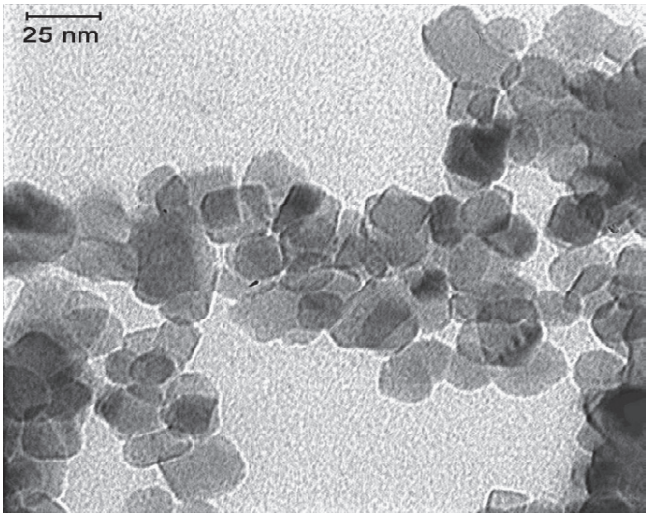

Fig. 6. shows the TEM image of the particles obtained at 800 °C

Figure 5 shows the TEM image of the particles obtained at 750 °C. Most of the powders were rectangle in shape. The average particles diameter was found to be approximately 21nm. This value was consistent with the result calculated by XRD (19nm) using Scherrer's formula

Figure 6 shows the TEM image of the particles obtained at 800 °C. The average particle diameter was found to be approximately 44 nm. These powders were agglomerated and they were not as homogeneous and uniform as previous powders.

4. CONCLUSION

Fine BST nanoparticles, with the average particle size of 21 nm, were successfully synthesized by a repeatable simple sol-gel process. XRD and TG/DTA results revealed that pure phase BST can be obtained above 750 °C. It has been shown that nanoparticles obtained at higher temperatures like 800 °C were more agglomerated and more than twice the size as those obtained at 750 °C. This innovative, simple and time-saving method offers a new strategy for fabrication of nanoscaled powders in other electronic materials.

5. REFERENCES

[1] BETHE K., WELZ F., Mater. Res. Bull., 6 (1971), 209.

[2] WANG J.Y., YAO X., ZHANG L.Y., Ceram. Int., 30 (2004), 1749.

[3] JANG H.M., JUN Y.H., Ferroelectrics., 193 (1997), 125.

[4] MAO C., DONG X., ZENG T., Matter. Lett., 61 (2007), 1633.

[5] SUASMORO S., PRATAPA S., HARTANTO D., SETYOKO D., DANI U.M., J. Eur. Ceram. Soc., 20 (2000), 309.

[6] KAO C.F., YANG W.D., Appl. Organometal. Chem., 13 (1999), 383.

[7] SHIIBASHI H., MATSUDA H., KUWABARA M., J. Sol-Gel Sci. Techn., 16 (1999), 129.

[8] KOMAROV A.V., PARKIN I.P., ODLYHA M., J. Mater. Sci., 31 (1996), 5033.

[9] ROEDER R.K., SLAMOVICH E.B., J. Am. Ceram. Soc., 82 (1999), 1665.

[10] TSAY J.D., FANG T.T., GUBIOTTI T.A., YING J.Y., J. Mater. Sci., 33 (1998), 3721.

[11] BELLAMY L.J., *The Infra-Red Spectra of Complex Molecules*, Methuen Co. Ltd., London, 1958.

[12] DURA N.P., CAPEL F., GUTIERREZ D., TARTAJ J., BANARES M.A., MOURE C., J. Mater. Chem., 11 (2001), 1828.

[13] TIAN H.Y., QI J.Q., WANG Y., WANG J., CHAN H.L.W., CHOY C.L., Nanotech, 16 (2005), 47.

* * *

N. Ramakoteswara Rao,
Department of Nanoscience & Technology, Swarnandra College of engineering& Technology, Narsapur, India.
rkrao.nathani@gmail.com