



## Synthesizing Nanocrystalline Barium Strontium Titanate Powders by Citrate Precursor Method

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*Nanocrystalline and well dispersed barium strontium titanate (BST) powders were prepared by a novel and simple citrate precursor method. This method involves direct crystallization of a white precursor from a stable solution in the citric acid (CA)-ethylene glycol (EG)-tetrabutyl titanate  $M_{2+}$  ( $M=Ba, Sr$ ) system under a specific pH value range. Subsequent heat treatment of the precursor at  $850^{\circ}\text{C}$  led to a pure phase BST powder. The crystalline phase and morphology of the BST powders were investigated by XRD. It was found that the BST powders synthesized by citrate precursor process were more homogeneous and uniform than that obtained by the citrate gel method.*

**Key words:** (Ba,Sr)TiO<sub>3</sub>; Nanocrystalline; Citrate precursor.

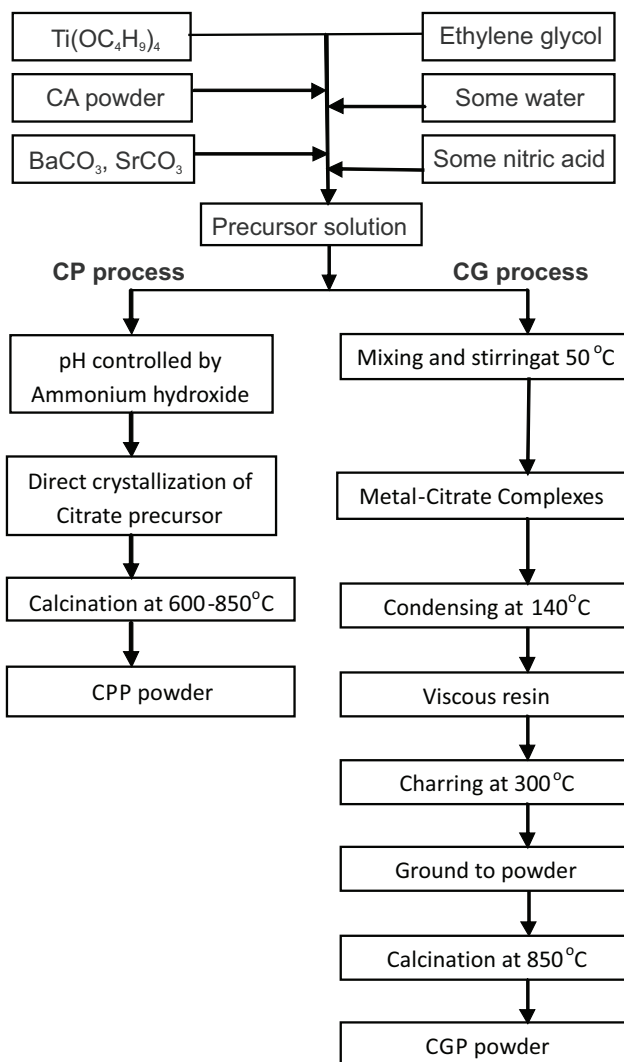
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**Introduction :** Ferroelectric BST is a kind of favourable electronic material for its high dielectric constant and alterable Curie temperature with composition (K. Bethe, F. Welz, Mater. Res. Bull. 6, 1971). There is increasing interest for the use of BST in piezoelectric sensors, dynamic random access memories (DRAM), microwave phase shifters and uncooled infrared detectors (X. Li. et. al., 1997, F. Selmi et. al., 1990) for its high dielectric, ferroelectric and pyroelectric properties. In order to attain the desired electrical characteristics, high chemical purity and 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 for the synthesis of the nanocrystalline BST. Conventional solid-state reaction is not suitable for preparing BST materials with high performance, as the calcining and sintering temperatures are too high. Compared to the conventional solid-state method, the synthesis of BST powder through chemical solution routes offers several advantages, such as high-purity, homogeneity and precise composition. There are a lot of chemical methods to prepare BST powders, such as coprecipitation, hydrothermal, polymeric precursor method and sol-gel process (R.W. Whatmore. et. al., 1987, D.S. Kang. et. al., 2003, F. Schrey. et. al., 1965,

R.K. Roeder. et. al., 1999). Stoichiometric deviation is the most crucial problem existing in the coprecipitation and hydrothermal process. Among others, sol-gel process is a favorable method for its low temperature synthesis of BST nanopowders with high-purity and homogeneity. Conventional sol-gel process involves three primary steps: dissolution, hydrolysis and condensation (M.P. Pechini, U.S. Pat., 1967). However, the amount of water used during the two initial processes is extremely critical and uncontrollable. Inadequate and excess water may lead to the unhydrolyzation and precipitation in the solution, respectively. Furthermore, the quality of final product extremely depends on the amount of water and the pH value. All of these largely restrain the widespread applications of sol-gel method. Thus, in order to synthesize BST nanopowders simply and unrestrictedly, it is necessary and important to improve the conventional sol-gel method. The present paper describes an innovative and simple citrate precursor process for the preparation of nanocrystalline BST powders at relatively low temperature without any water. The nanosized nature of the BST powders was investigated by transmission electron microscopy (TEM). Fine and slight agglomerated powders are very useful and important to be sintered.

## Experimental :

Synthesis of  $Ba_{0.70}Sr_{0.30}TiO_3$  nanocrystalline powders  $Ba_{0.70}Sr_{0.30}TiO_3$  powders were synthesized by the citrate precursor method as summarized in Fig. 1. For the preparation of the precursor solution, barium carbonate (99.0%), strontium carbonate (99.0%), tetrabutyl titanate (98%), citrate acid (99.5%), and ethylene glycol (EG) were used as starting materials. First, 0.1 mol of  $Ti(C_4H_9O)_4$  was dissolved into 2 mol of ethylene glycol. The mixture was stirred for about 5 min until it became transparent and yellow. Subsequently, 0.5 mol CA powders were directly added to this solution. A little water (about 0.5 ml water per gram of CA) was blended into the solution to help dissolve CA. A bit of white precipitate was observed at first but immediately dissolved after they were stirred for 30 min on a magnetic stirrer and the solution came back to clear. Then, stoichiometric  $BaCO_3$  and  $SrCO_3$  powders were added to this solution (Ba/Sr ratio was fixed at 70/30). Three drops of nitric acid  $HNO_3$  for every 100 ml of mixture were added to the sample to catalyze the dissolving of the carbonates and esterification between CA and EG. The mixture was stirred continuously until it became a clear solution, pale brown in color. Then, ammonium hydroxide solution was added to the precursor solution to adjust the pH value. With different pH values, the states of the solution were different. The results are shown in Table 1. When the pH was in the range of 2.3-3.2, the solution would transform into white crystals which will be here in after referred to as the precursor. After drying in air for 2 days, the precursor was calcined at 600-850°C for 2 hours to synthesize  $Ba_{0.70}Sr_{0.30}TiO_3$  powders, here in after referred to as the CPP, powder. For comparison, nanocrystalline BST powders were also synthesized by the traditional CG process. In this process, the precursor solution was immersed in a basin with hot silicon oil (50-60°C) and stirred for 12 hours. Then it was put into an oven and dried at 140°C to promote polymerization and remove excess solvents. With continuous heating, the solution became a viscous resin with a change in color from pale brown to deep brown. Charring the resin at 300°C for 2 h in an electric furnace resulted in a porous and black solid mass. This solid mass was lightly ground into a powder and calcined at 850°C for 2 h in a muffle furnace to synthesize BST powders, here in after referred to as the CGP powder.



## Results and discussion :

Table 1 shows the results of the solution state under different pH values. It can be seen that the precursor could crystallize from the solution in the specific pH value range of 2.3-3.2. Both interactions between the metal ions and the organic groups and pH value of the initial solution are of utmost importance to obtain the direct crystallization of a precursor from a clear solution.

Arima et al<sup>9</sup> suggested that as the coexistence of barium and titanium ions in the Ba-Ti-CA/EG solution, the two metal ions would interact strongly with carboxylic-acid groups of CA. By adjusting the pH value of the solution, (Ba,Ti) citrates could crystallize.

**Table 1**

**The results of the solution state under different pH values**

No.	pH	State (cry = crystallization, sol. = solution)
1.	0.5	Sol.
2.	1.0	Sol.
3.	2.0	Sol.
4.	2.3	Sol.
5.	3.2	Sol.
6.	3.5	Sol.
7.	4.2	Cry.
8.	6.4	Sol.
9.	10.0	Sol.

**Conclusion :**

Fine and slight agglomerated BST nanoparticles, were successfully synthesized by a simple citrate precursor process. The pure phase BST could be obtained at 850°C. The BST powders synthesized by the CP process were more homogeneous and uniform than that obtained by the dry route. This innovative method, simple and time saving, will offer a new strategy for preparing nano scaled powders in other electronic materials.

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