A NOVEL LOW TEMPERATURE SYNTHESIS OF SrTiO$_3$ FROM Sr-OXALATE AND TiO$_2$

P.K. Roy, J. Bera

Department of Ceramic Engineering, National Institute of Technology
Rourkela-769008, India

Abstract

TiO$_2$ and Sr(NO$_3$)$_2$ raw materials were used for the preparation of SrTiO$_3$. Sr-oxalate is precipitated from Sr(NO$_3$)$_2$ solution onto the surface of suspended TiO$_2$ particles. Crystallization of SrTiO$_3$ from the precursor was investigated by TGA, DTA and XRD analysis. SrTiO$_3$ formation occurs at much lower temperature, from 800°C onwards, due to the fine particle size of intermediate SrCO$_3$. The precursor completely transforms into SrTiO$_3$ at 1100°C. About 27 to 52 nm size SrTiO$_3$ crystallites are produced in the range 800-900°C, due to the lower calcination temperature and better homogeneity of the precursor.

*Keywords***:** A. Ceramics; B. Nanostructures; C. Electronic materials; D. Chemical synthesis.

1. Introduction

SrTiO$_3$ is a technologically important perovskite electro-ceramic material. Important applications are its use as grain-boundary barrier layer capacitor (GBBLC) materials [1], as thin film in dynamic random access memories (DRAM's) [2], as substrate for the hetero-epitaxial growth of high T$_c$-superconductors [3], as oxygen gas sensor [4], as varistor [5] and as material in low-voltage electron-excitation display [6]. It is typically prepared by solid-state reaction [7] or by chemical solution methods like; oxalic co-precipitation [8, 9], sol-gel [10], hydrothermal [11], auto-combustion synthesis [12] etc. Chemical solution methods produce more homogeneous, finer particle size and low impurity levels powders than that produced by solid-state method. On the other hand the solid-state synthesis has advantages with respect to the use of low-cost raw materials and simple processing steps. SrCO$_3$ and TiO$_2$, used by solid-state route, are relatively cheaper than their nitrate/chloride/alkoxide salts, which are required for chemical route. In the present synthesis, TiO$_2$ and Sr(NO$_3$)$_2$ raw materials were used for the preparation of SrTiO$_3$ to get some of the benefits of both the solid-oxide and chemical route. As, Ti-salts are relatively costlier than Sr-salts; use of TiO$_2$ can effectively reduce the powder synthesis cost. It has been calculated that in this process the cost is about 20% lower then solid state route. Secondly, Sr(NO$_3$)$_2$ is used to precipitate Sr-oxalate from its water solution onto the surface of suspended TiO$_2$ particles, which gives a more homogeneous mixing of raw materials than that obtained in solid powder mixing.

2. Experimental procedure

The starting materials used in the present work included; Sr(NO$_3$)$_2$ (>99%, Loba Chemie Pvt. Ltd., India), TiO$_2$ (>99%, E-Merck, India, Particle size: d$_{10}$=0.27µm, d$_{50}$=0.35µm, d$_{90}$=0.48µm) and (COOH)$_2$.2H$_2$O (>99.5%, S. D. Fine-Chem Ltd., India). An aqueous solution of 0.12 molar Sr(NO$_3$)$_2$ was prepared using deionized water. The exact molarity of the solution was determined from the chemical analysis of the nitrate solution using Solochrome Black-T indicator and standard EDTA solution. Required amount (Sr/Ti = 1:1) of TiO$_2$ powder was added to the Sr(NO$_3$)$_2$ solution with constant stirring. The

suspension was treated in ultrasonic bath (for 10 minutes) to break TiO_2 agglomerates. Required amount of oxalic acid (0.4 molar solution) was added drop wise into the mixture under vigorous stirring. The pH of the resultant mixture was adjusted to 5, 7, and 9 respectively by adding ammonia solution at room temperature. In the second set of experiment, the ammonia solution was added to get pH=7 after maintaining the temperature of the bath 50, 70 and 90ºC respectively. This process precipitated strontium oxalate on the surface of fine TiO_2 (acting as seed) particles by heterogeneous nucleation [13]. The resulting precipitates were then washed repeatedly using deionized water, followed by drying at 40ºC for 48 hours. The decomposition behavior of precursor was characterized using thermo-gravimetric analysis and differential thermal analysis, at a heating rate of 10ºC /minute in air from room temperature up to 1300ºC. The precursor was calcined in air for 1 hour at various temperatures up to 1200ºC, followed by phase identification performed at room temperature using a Cu-K_α X-Ray Diffractometer (PW-1830, Philips, Netherlands). To quantify the $SrTiO_3$ and intermediate $SrCO_3$ concentrations, calcined powders were uniformly mixed with internal standard CaF_2 powder and the resulting mixture was analyzed using a step size of 0.02º, 2θ with 10 second/step. The relative weight fractions of $SrTiO_3$ and $SrCO_3$ were quantified from the ratio of [110] peak area of $SrTiO_3$ and [021] peak area of $SrCO_3$, with the [111] peak area of CaF_2, according to the process described by S. Kumar & G. L. Messing [14]. On the basis of XRD line broadening at half maxima of the above said peaks, crystallite sizes of $SrTiO_3$ in the calcined powders were estimated using the Scherrer equation [15].

3. Results and Discussion

Fig. 1 shows the XRD patterns of precursors obtained at different pH-room temperature and at different temperature in pH=7. It shows that the precursor powders contain strontium oxalate hydrate and TiO_2 in anatase form. Strontium oxalate hydrate phase was identified as a mixture of $SrC_2O_4.1H_2O$ (PDF No. 20-1203) and $SrC_2O_4.2.5H_2O$ (PDF No. 20-1204). At pH= 5, it contains $SrC_2O_4.1H_2O$, small amount carbonate hydrate (PDF No. 14-0910) and very low amount of $SrC_2O_4.2.5H_2O$. As pH increased, the amount of $SrC2O4.2.5H2O$ is increased. But at pH=7, when temperature is increased $SrC2O4.2.5H2O$ content is decreased and at 90ºC it contains only $SrC_2O_4.1H_2O$.
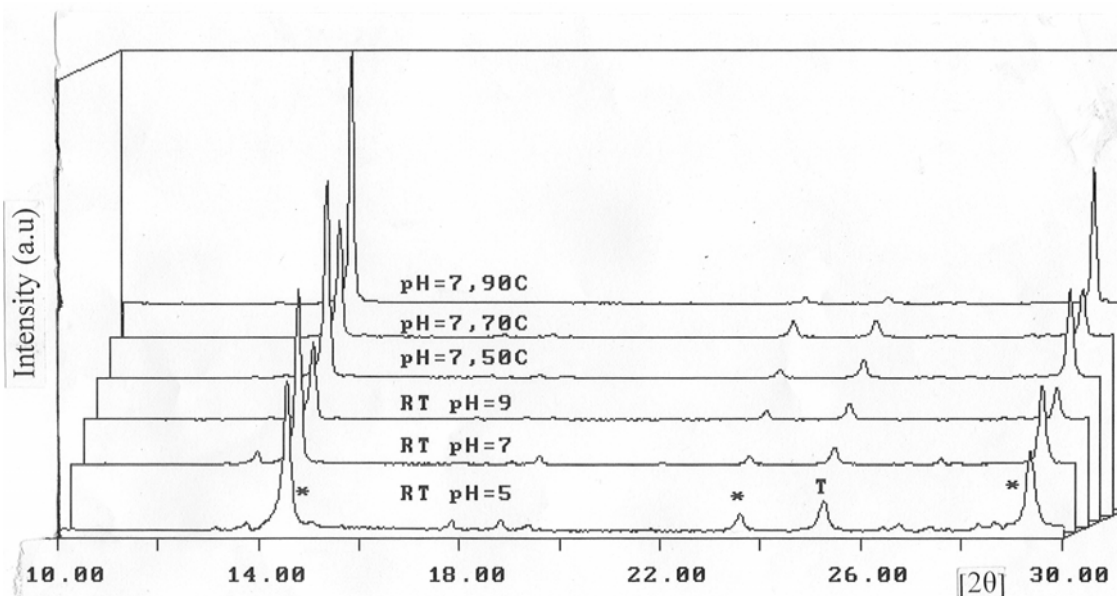

Fig. 1.   XRD patterns of Raw precursor obtained at different pH in room temperature and at different temperature in pH=7. The abbreviation for the phases: * = $SrC_2O_4.xH_2O$, T = TiO_2,
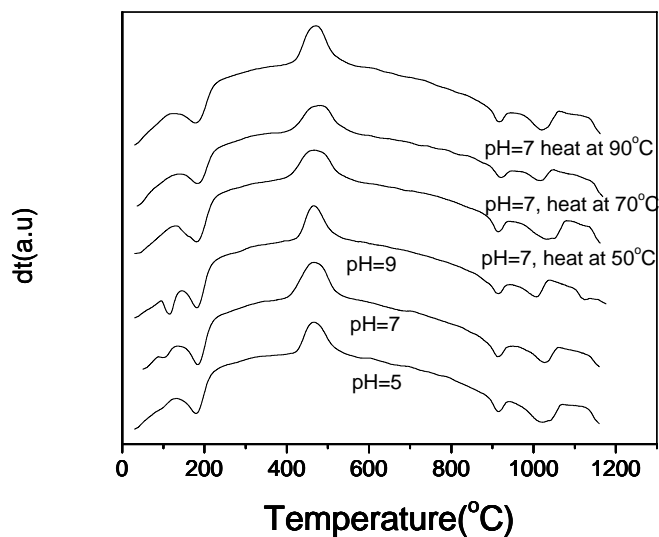
Fig. 2 DTA tracing of the different precursor powders.

Fig. 2 shows the DTA tracing of the precursor powders prepared at 30^oC with pH= 5, 7, and 9, and at a constant pH=7 with different temperatures 50^oC, 70^oC, and 90^oC respectively. TG-graph (Fig.3) shows the loss of weight in three-stages. The first major weight loss in the temp range 150 to 350^oC, corresponds to a two stage endothermic reaction in the DTA curve. This two-stage endothermic reaction is due to the release of crystalline water of Sr-oxalate hydrate, as per reaction:
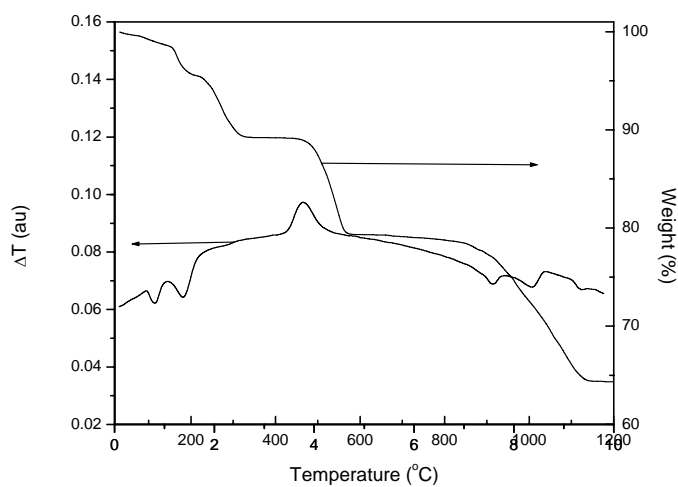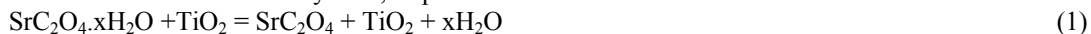
$$SrC_2O_4.xH_2O + TiO_2 = SrC_2O_4 + TiO_2 + xH_2O \qquad (1)$$

Fig.3 DSC/TG tracing of ph=7 precursor

XRD analysis of raw powder (Fig. 1) shows that it is a mixture of both $SrC_2O_4.1H_2O$ and $SrC_2O_4.2.5H_2O$ along with the anatase form of TiO_2. This identification also suggests that the two stage dehydration reactions may be for the decomposition of those two types of oxalate-hydrate phases. The two-stage decomposition of oxalate-hydrate was also reported by E.Knaepen et.all [16].

The second stage weight loss is due to the formation of $SrCO_3$ from SrC_2O_4 as per reactions:

$$SrC_2O_4 + TiO_2 = SrCO_3 + CO + TiO_2 \qquad (2)$$
$$CO + O_2 = CO_2 \qquad (3)$$

The endothermic peak corresponding to the carbonate formation reaction (Reaction 2), has merged with the next exothermic peak (Reaction 3). An XRD analysis of 700°C-DTA samples (Fig. 4) shows the presence of $SrCO_3$ and TiO_2 only.

The third weight loss, started from about 800°C, is due to the decomposition of $SrCO_3$ and formation of $SrTiO_3$. $SrCO_3$ also produces a sharp endothermic phase transformation at 936°C, from orthorhombic to rhombohedral space group [17]. The endothermic peak at 1047°C is due to the vigorous decomposition of $SrCO_3$ and simultaneous formation of $SrTiO_3$. The total weight losses of precursors produced at pH 5, 7, 9 are 32.68%, 32.73%, and 35.66% respectively. The weight loss is highest at pH=9 precursor, because it contains highest amount of $SrC_2O_4.2.5H_2O$. The total weight losses at constant pH=7 in different temperatures 50°C, 70°C, and 90°C are 34.40%, 32.73% and 31.62% respectively. Here the weight loss is lower at 90°C due presence of only $SrC_2O_4.1H_2O$ content.
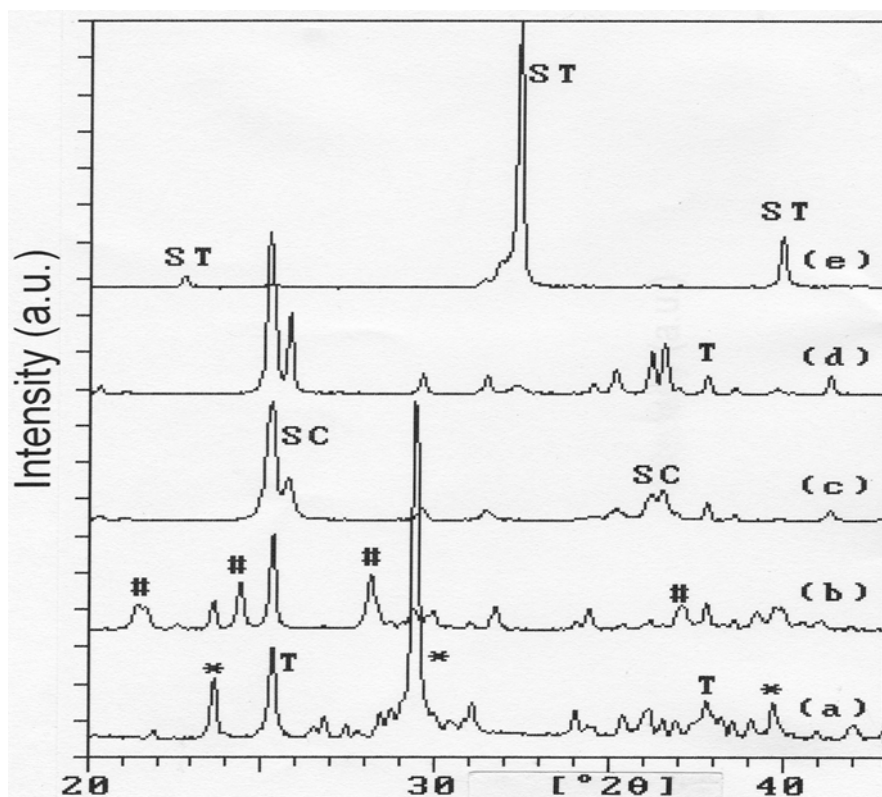

Fig. 4. XRD patterns of (a) Raw precursor and precursors calcined at (b) 400°C (c) 700°C (d) 900°C and (e) 1100°C for 1 hour (pH=7). The abbreviation for the phases: * = $SrC_2O_4.xH_2O$, # = SrC_2O_4, T = TiO_2, Sc = $SrCO_3$ and ST = $SrTiO_3$.

To understand the fundamental issues of $SrTiO_3$ formation in the present case, the precursors were heated in air at different temperatures and then were analyzed by XRD. Fig. 2 shows the XRD patterns of the precursor at pH=7 and that heated at different temperatures. The precursor powder contains strontium oxalate hydrate and TiO_2 phases. Only the relative intensity of the peak at 29.42º 2θ or [200] reflection of $SrC_2O_4.1H_2O$ was very high with respect to its standard, which may be due to the defect inter-grown structure of oxalate hydrate phases. That peak intensity drastically decreases after a nominal heat treatment. For example 400ºC sample (Fig. 2) shows a low intensity [200] peak, comparable to that of the standard. 400ºC sample shows, the formation of SrC_2O_4 in the system along with TiO_2 and small amount of un-decomposed oxalate hydrate phases. Above 500ºC, $SrCO_3$ phase appears in the system due to the oxidation of oxalate .700ºC sample (Fig. 2) shows the presence of $SrCO_3$ and TiO_2 phases only. The precursor was completely transformed into single phase $SrTiO_3$ at 1100ºC for 1-hour calcination and it was X-Ray pure with lattice parameter a_0=3.9057Å.. To check the intermediate phase formation, the samples were also heat-treated at 50ºC interval in the temperature range 500-900ºC, without holding at the peak temperature. No traces of intermediate SrO and/or Sr_2TiO_4, $Sr_3Ti_2O_7$ phases were detected by XRD at any stages of transformation. This indicates that the homogeneity of the precursor was fairly good.
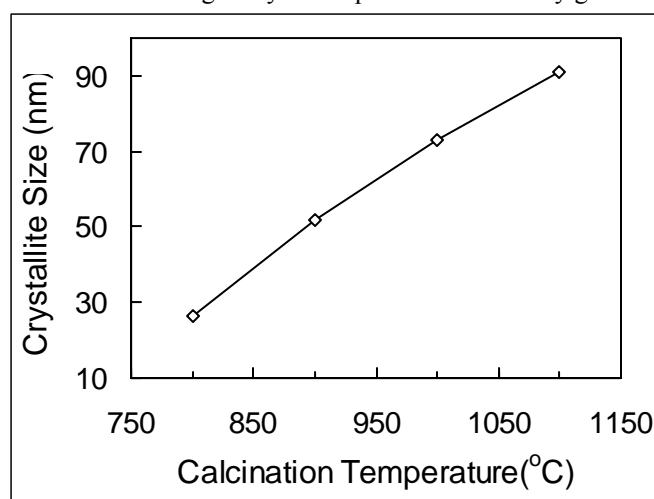

Fig. 5.   Average crystallite size of $SrTiO_3$ estimated on the basis of
peak broadening as a function of calcinations temperature.

The $SrTiO_3$ powders synthesized in this process was characterized with respect to crystallite size developed as a function of calcination temperature. Fig. 4 plots the average crystallite size as a function of calcination temperature. As expected, crystallite size increases with increasing calcination temperature. The increase in crystallite size may be due to the partial sintering and growth of fine $SrTiO_3$ crystallites. So, $SrTiO_3$, with crystallite size 70-90nm, can be synthesized by calcining the precursor at 1000-1100ºC/1hr.

4. Conclusion:

1. $SrTiO_3$ powder has been prepared from Sr-oxalate and TiO_2 precursors, instead of using titanyl-oxalate.
2. Sr-oxalate was precipitated from nitrate solution onto the surface of suspended TiO_2 powders.
3. It is evident that precursor, upon heating, dehydrates in two stages, may be due to the presence of two different types of Sr-oxalate hydrates.
4. Decomposition of $SrCO_3$ and simultaneous $SrTiO_3$ formation occur at much lower temperature, from 800ºC onwards, due to the fine particle size of the $SrCO_3$ and presence of acidic TiO_2 in the mixture.
5. About 90 nm size $SrTiO_3$ crystallites are produced at 1100ºC/1hr, due to the lower calcination temperature.

6. In this process the cost is about 20% lower then solid state route.

5. References:

[1] M. Fujimoto, W.D. Kingery, J. Am. Ceram. Soc. 68 (1985) 169.
[2] D. Chambonnot, C. Andry, A. Fages-Bonnery, C. Mer, C. Fages, J. Perriere,   J. Phys. France, 8
   (1998) 213-216.
[3] M. Kawai, S. Watanabe, T. Hanada, J. Cryst. Growth, 112 (1991) 745.
[4] J. Gerblinger, H. Meixner, Sens. Actuators, B 4(1991) 99.
[5] S.H. Kim, J.D. Byun, W. Park et al., J. Mater. Sci. 34 (1999) 3057.
[6] H. Yamamoto, S. Okamoto, H. Toki, K. Tamura, S. Itoh, The third Int. Conf. on the Sci. and Tech. of
     Display Phosphors, 1997,p17.

[7] A. Wold, K. Dwight, J. Solid State Chem. 88 (1990) 229-238.
[8] K. Kudaka, K. Hzumi, K. Sasaki, Am. Cera. Soc. Bull. 61 (1982) 1236-1240.
[9] G. Pfaff, F. Schmidt, W. Ludwig, A. Feltz, J. Thermal. Anat. 33(1988) 771-779.
[10] G. Pfaff, J. Mater. Chem. 3 (1993) 721.
[11] D. Chem, X. Jiao, M. Zhang, J. Eur. Chem. Soc. 20 (9)(2000) 1261-1265.
[12] J. Poth, R. Haberkorn, H.P. Beck, J. Eur. Cera. Soc. 20 (2000) 707-713.
[13] J. Bera, D. Sarkar, J. Electroceramics, 11 (2003) 131.
 [14] S. Kumar, G.L. Messing, J. Am. Cerm. Soc. **77**[11] (1994) 2940.
[15] H.P. Klug and L.E. Alexander, Crystallite Size Determination from Line Broadening. Wiley, New
      York, 1954, p. 491.
[16] E. Knaepen, J. Mullens, J. Yperman, L. C. Van Poucke, Thermochimica Acta, 248 (1996) 213-227
[17] R. C. Evans, An Introduction to Crystal Chemistry, Cambridge University Press, Cambridge, UK,
      1966, 410