



A NOVEL LOW TEMPERATURE SYNTHESIS OF SrTiO₃ FROM Sr-OXALATE AND TiO₂

P.K. Roy and J. Bera

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

ABSTRACT

TiO₂ and Sr(NO₃)₂ raw materials were used for the preparation of SrTiO₃. Sr-oxalate is precipitated from Sr(NO₃)₂ solution onto the surface of suspended TiO₂ particles. Crystallization of SrTiO₃ from the precursor was investigated by TGA, DTA and XRD analysis. SrTiO₃ formation occurs at much lower temperature, from 800°C onwards, due to the fine particle size of intermediate SrCO₃. The precursor completely transforms into SrTiO₃ at 1100°C. About 27 to 52 nm size SrTiO₃ crystallites are produced in the range 800-900°C, due to the lower calcination temperature and better homogeneity of the precursor.

Keywords: Ceramics; SrTiO₃; Novel synthesis; Nano-crystalline

1. INTRODUCTION

SrTiO₃ is a technologically important perovskite electro-ceramic material. Important applications are its use as grain-boundary barrier layer capacitor (GBBL) 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. SrCO₃ and TiO₂, used by solid-state route, are relatively cheaper than their nitrate/chloride/alkoxide salts, which are required for chemical route. In the present synthesis, TiO₂ and Sr(NO₃)₂ raw materials were used for the preparation of SrTiO₃ 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 TiO₂ can effectively reduce the powder synthesis cost. It has been calculated that in this process the cost is about 20% lower than solid state route. Secondly, Sr(NO₃)₂ is used to precipitate Sr-oxalate from its water solution onto the surface of suspended TiO₂ particles, which gives a more homogeneous mixing of raw materials than that obtained in solid powder mixing.

2. EXPERIMENTAL

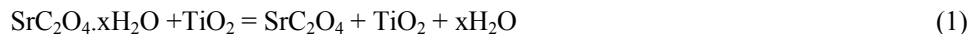
The starting materials used in the present work included; Sr(NO₃)₂ (>99%, Loba Chemie Pvt. Ltd., India), TiO₂ (>99%, E-Merck, India, Particle size: d₁₀=0.27µm, d₅₀=0.35µm, d₉₀=0.48µm) and (COOH)₂.2H₂O (>99.5%, S. D. Fine-Chem Ltd., India). An aqueous solution of 0.12 molar Sr(NO₃)₂ was prepared using 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 TiO₂ powder was added to the Sr(NO₃)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 90°C 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 40°C for 48 hours. The decomposition behavior of precursor was characterized using thermo-gravimetric analysis and differential thermal analysis, at a heating rate of 10°C /minute in air from room temperature up to 1300°C. The precursor was calcined in air for 1 hour at various temperatures up to 1200°C, 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 0.02°, 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].

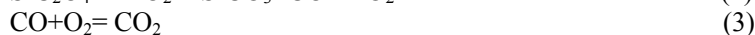
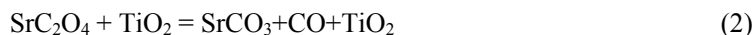
3. RESULTS AND DISCUSSION

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 $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$ (PDF No. 20-1203) and $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ (PDF No. 20-1204). At pH= 5, it contains $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$, small amount carbonate hydrate (PDF No. 14-0910) and very low amount of $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$. As pH increased, the amount of $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ is increased. But at pH=7, when temperature is increased $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ content is decreased and at 90°C it contains only $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$.

Fig. 2 shows the DTA tracing of the precursor powders prepared at 30°C with pH= 5, 7, and 9, and at a constant pH=7 with different temperatures 50°C, 70°C, and 90°C 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°C, 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:



XRD analysis of raw powder (Fig. 1) shows that it is a mixture of both $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$ and $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$ 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.al. [16]. The second stage weight loss in the temperature range 470-620°C is due to the formation of SrCO_3 from SrC_2O_4 as per reactions:



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 918°C, from orthorhombic to rhombohedral space group [17]. The endothermic peak at 1018°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, and 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 $\text{SrC}_2\text{O}_4 \cdot 2.5\text{H}_2\text{O}$. The total weight losses of precursors produced 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 $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$ content.

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. 4 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 $29.42^\circ 2\theta$ or [200] reflection of $\text{SrC}_2\text{O}_4 \cdot 1\text{H}_2\text{O}$ 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 400°C sample (Fig. 4) shows a low intensity [200] peak, comparable to that of the standard. 400°C 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 500°C, SrCO_3 phase appears in the system due to the oxidation of oxalate. 700°C sample (Fig. 4) shows the presence of SrCO_3 and TiO_2 phases only. The precursor was completely transformed into single phase SrTiO_3 at 1100°C for 1-hour calcination and it was X-Ray pure with lattice parameter $a_0 = 3.9057 \text{ \AA}$. To check the intermediate phase formation, the samples were also heat-treated at 50°C interval in the temperature range 500-900°C, without holding at the peak temperature. No traces of intermediate SrO and/or Sr_2TiO_4 , $\text{Sr}_3\text{Ti}_2\text{O}_7$ phases were detected by XRD at any stages of transformation. This indicates that the homogeneity of the precursor was fairly good.

The SrTiO_3 powders synthesized in this process was characterized with respect to crystallite size developed as a function of calcination temperature. Fig. 5 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 27 to 52 nm size SrTiO_3 crystallites are produced in the range 800-900°C.

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FIGURES

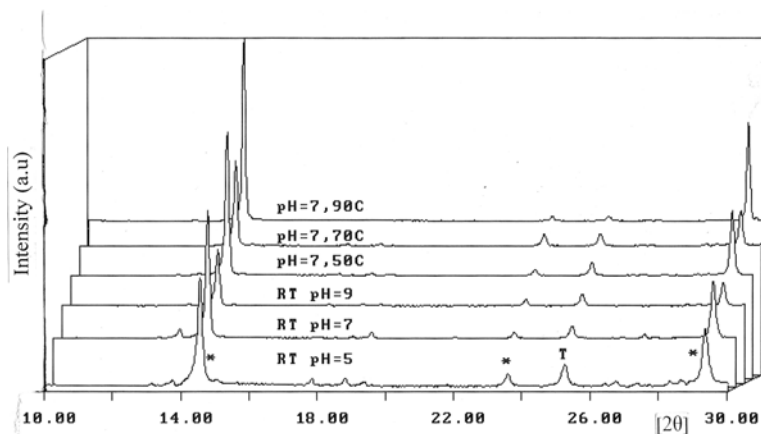


Fig. 1. XRD patterns of Raw precursor obtained at different pH in room temperature and at different temperature in pH=7. The abbreviation for the phases: * = $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, T = TiO_2 .

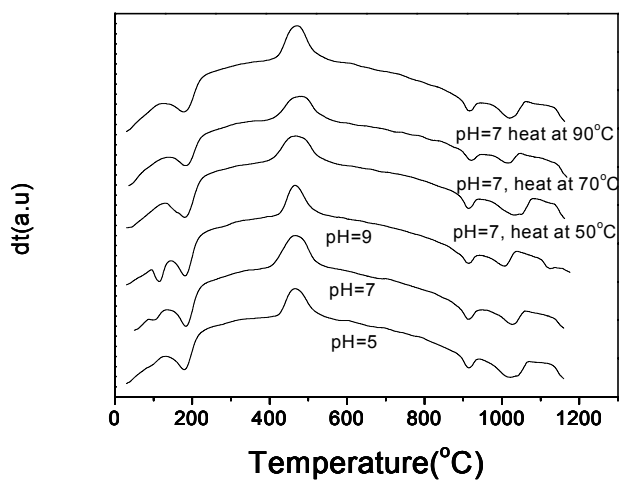


Fig. 2 DTA tracing of the different precursor powders.

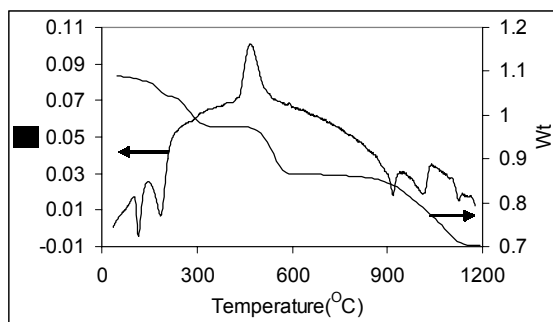


Fig.3 DSC/TG tracing of ph=7 precursor

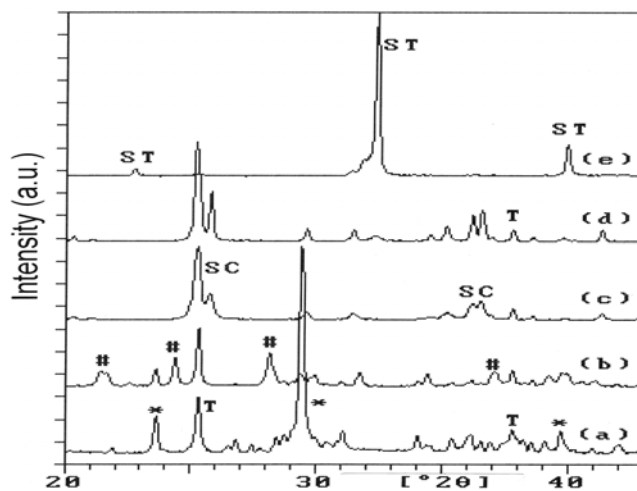


Fig. 4. XRD patterns of (a) Raw precursor and precursors calcined at (b) 400°C (c) 700°C (d) 900°C and (e) 1100°C for 1 hour (pH=7). The abbreviation for the phases: * = $\text{SrC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, # = SrCO_3 , T = TiO_2 , Sc = SrCO_3 and ST = SrTiO_3 .

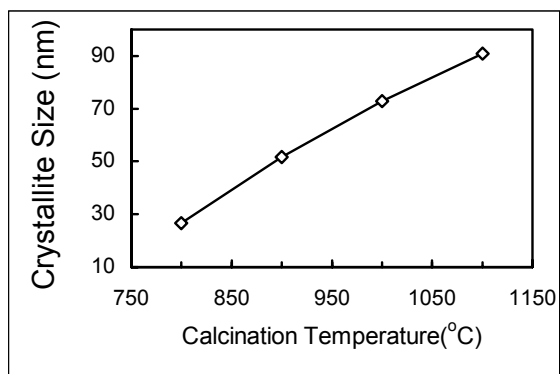


Fig. 5. Average crystallite size of SrTiO_3 estimated on the basis of peak broadening as a function of calcinations temperature.