Formation 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

SrTiO$_3$ powder has been prepared from Sr-oxalate and TiO$_2$ precursors, instead of using titanyl-oxalate. Sr-oxalate was precipitated from nitrate solution onto the surface of suspended TiO$_2$ powders. Crystallization of SrTiO$_3$ from the precursor was investigated by TGA, DTA and XRD analysis. 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. Dehydrated precursor then decomposes into SrCO$_3$ and TiO$_2$ mixture. Decomposition of SrCO$_3$ and simultaneous SrTiO$_3$ formation occur at much lower temperature, from 800°C onwards, due to the fine particle size of the SrCO$_3$ and presence of acidic TiO$_2$ in the mixture. The precursor completely transforms into SrTiO$_3$ at 1100°C. About 90 nm size SrTiO$_3$ crystallites are produced at 1100°C/1hr, due to the lower calcination temperature and better homogeneity of the precursor.

---

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. 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. This type of SrTiO$_3$

---

powder synthesis has not been reported earlier in the literature, except for $BaTiO_3$ powder synthesis reported recently by this group [13].

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 $(COOH)_2.2H_2O$ (>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 6-7 by adding ammonia solution. 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 TG-DSC tracing of the precursor powder. TG-graph shows the loss of weight in three-stages. The first major weight loss of about 7.92% in the temp range 150 to 350ºC, corresponds to a two stage endothermic reaction in the DSC curve. This two-stage endothermic reaction is due to the release of crystalline water of Sr-oxalate hydrate, as per reaction:

$$SrC_2O_4.xH_2O +TiO_2 = SrC_2O_4 + TiO_2 + xH_2O \qquad (1)$$
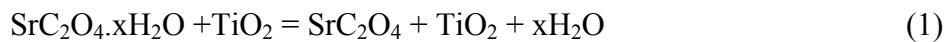
The reaction should produce a theoretical wt. loss of 6.58%, if Sr-oxalate is monohydrate ($SrC_2O_4.1H_2O$). The experimental wt. loss (7.92%) is higher than that. Possible reason

may be, Sr-oxalate hydrate phase or some fraction of the phase has higher amount of crystalline water than monohydrate. XRD analysis of raw powder (Fig. 2) 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. The excess wt. loss thus suggests that the oxalate hydrate may be a mixture of about 85% $SrC_2O_4.1H_2O$ and 15% $SrC_2O_4.2.5H_2O$ phases. 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].
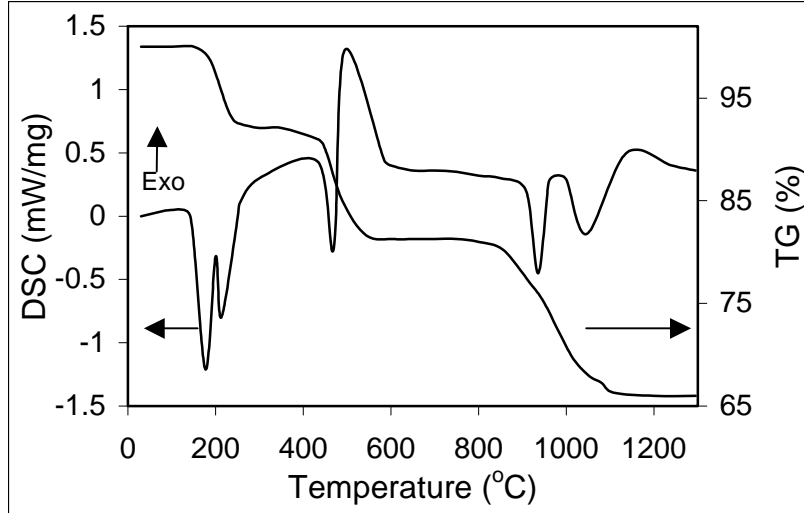

Fig. 1. DSC/TG tracing of precursor powder

The second stage weight loss (about 10.92%) 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 theoretical weight loss due to above reactions is 10.09% (for a mixture of 15% $SrC_2O_4.2.5H_2O$ & 85% $SrC_2O_4.1H_2O$). The experimental weight loss is slightly higher, which may be due to the decomposition of small amount of highly reactive $SrCO_3$. Reaction-(2) is an endothermic reaction. A fine endothermic peak at 469ºC is corresponding to that carbonate formation reaction. Simultaneously CO is converted exothermically to CO_2 by combining with O_2 from air. The huge exothermic peak followed by the endothermic one is due to the reaction-(3). An XRD analysis of 700ºC-DTA samples (Fig. 2) shows the presence of $SrCO_3$ and TiO_2 only.

The third weight loss, started from about 800ºC, is due to the decomposition of $SrCO_3$ and formation of $SrTiO_3$. $SrCO_3$ also produces a sharp endothermic phase transformation at 936ºC, from orthorhombic to rhombohedral space group [17]. The endothermic peak at 1047ºC is due to the vigorous decomposition of $SrCO_3$ and simultaneous formation of $SrTiO_3$.
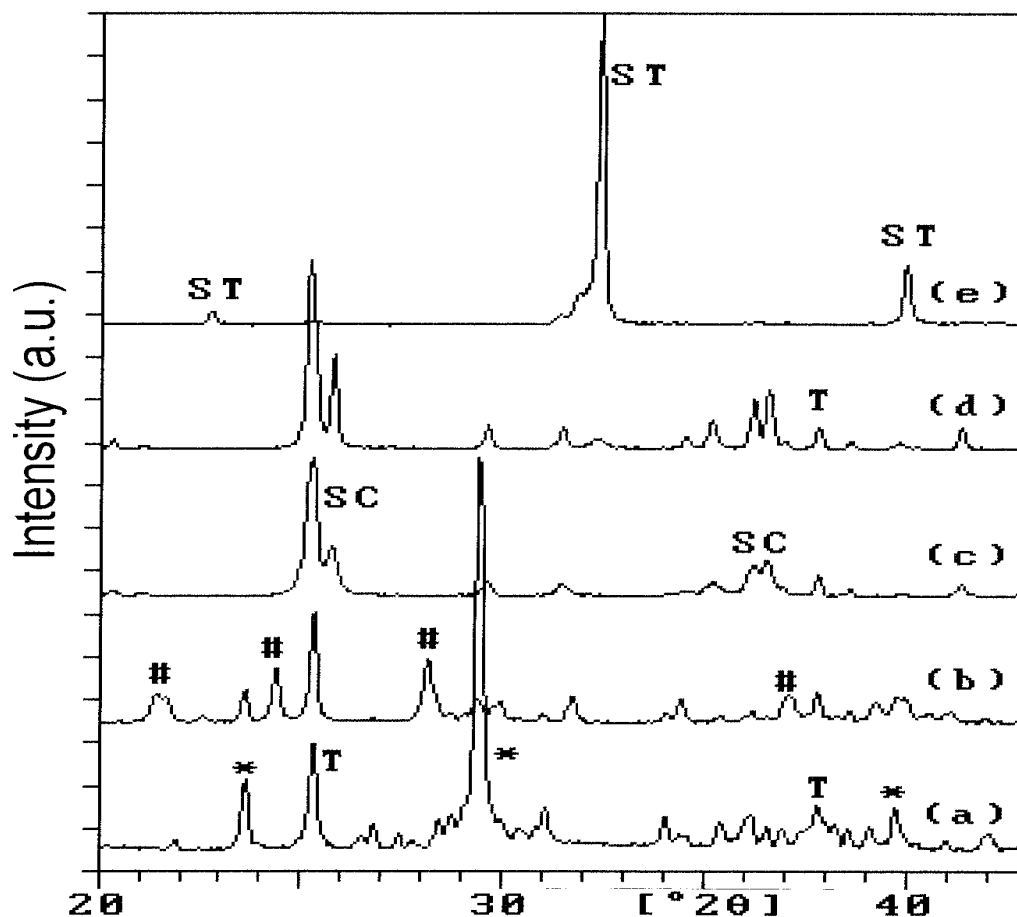
Fig. 2. XRD patterns of (a) Raw precursor and precursors calcined at (b) 400°C (c) 700°C (d) 900°C and (e) 1100°C for 1 hour. The abbreviation for the phases: * = $SrC_2O_4.xH_2O$, # = SrC_2O_4, T = TiO_2, Sc = $SrCO_3$ and ST = $SrTiO_3$.

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 and that heated at different temperatures. The precursor powder contains strontium oxalate hydrate and TiO_2 phases. 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). Only the relative intensity of the peak at 29.42° 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 400°C sample (Fig. 2) 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 (reaction 2). 700°C 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 1100°C for 1-hour calcination and it was X-Ray pure with lattice

parameter $a_0=3.9057\text{Å}$.. To check the intermediate phase formation, the samples were also heat-treated at $50^{\circ}C$ interval in the temperature range 500-900$^{\circ}C$, 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.

XRD quantitative estimation of $SrCO_3$ and $SrTiO_3$ on the samples heated at different temperature for one hour shows (Fig. 3) that the quantity of $SrCO_3$ slowly decreases and $SrTiO_3$ slowly increases up-to 800$^{\circ}C$. Decomposition of carbonate and formation of titanates are rapid from 800$^{\circ}C$ to 1000$^{\circ}C$. The amount of $SrCO_3$ (peak area) decreases rapidly after 800$^{\circ}C$. The rapid decomposition of $SrCO_3$ after 800$^{\circ}C$ may be due to the two following reasons. Firstly, may be due to small crystallite size of the $SrCO_3$ and presence of acidic TiO_2 in the mixture. Secondly, the polymorphic transformation of $SrCO_3$ near 936$^{\circ}C$ may accelerate its decomposition due to the formation of defects in the crystallites during the transformation. It is possible to prepare phase pure $SrTiO_3$ by calcining the precursor at 1000$^{\circ}C$ for 8-10 hours.

The concentration of $SrTiO_3$ formed was used as a measure of the final stage of the transformation. Taking the transformation to obey first-order reaction kinetics, the velocity constant (k) is determined for different temperatures and then activation energy (E) is evaluated from the Arrhenius plot (Fig. 4) of 'log k' against 1/T, according to shrinking core model [18]. Fig. 4 shows the Arrhenius type dependency of reaction rate on calcination temperature for $SrTiO_3$ phase formation. Transformation reaction in the temperature range has activation energy of 39.9 Kcal/mole and that may be rate-controlled by Sr^{2+} ion diffusion through the product layer [19].
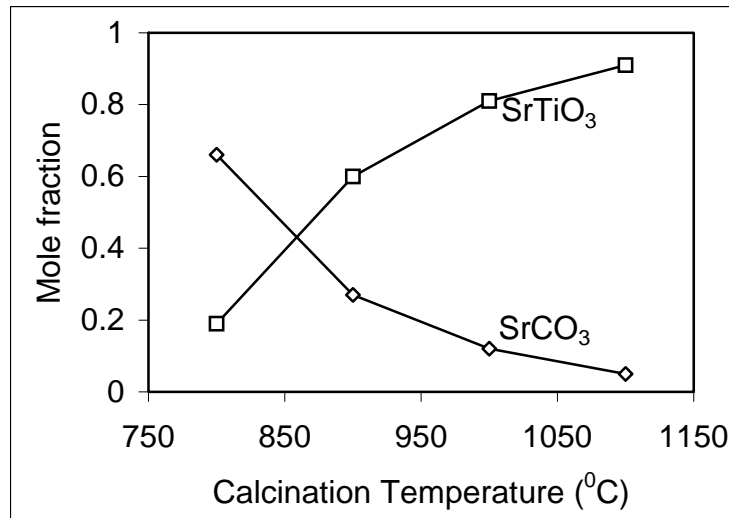

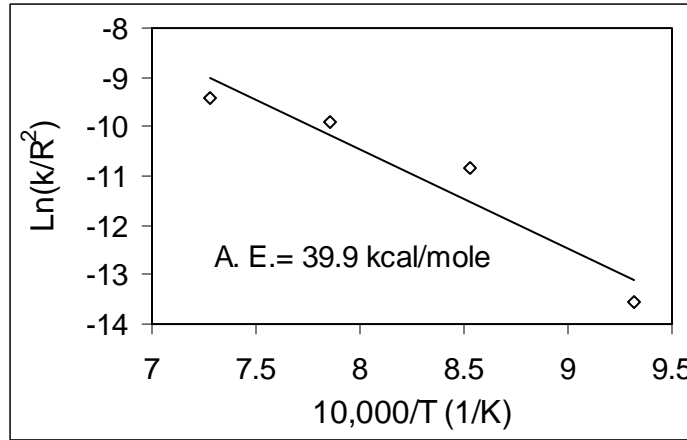Fig. 3. Non-isothermal transformation kinetics of precursor in static air.

Fig. 4.   Arrhenius dependence of reaction rate on calcination
            temperature for the transformation of precursor to $SrTiO_3$.

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 70-90nm, can be synthesized by calcining the precursor at 1000-$1100^oC/1hr$.
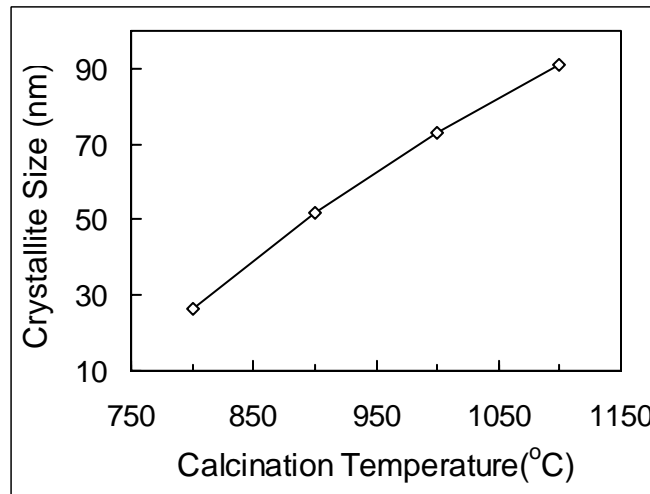

Fig. 5.   Average crystallite size of $SrTiO_3$ estimated on the basis of
          peak broadening as a function of calcinations temperature.

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

[18] Terry A. Ring, Fundamentals of Ceramic Powder Processing and Synthesis, Academic Press, Inc. 1996, p. 174.

[19] A. Bauger, J. Mutin, and J.C. Niepce, J. Mater. Sci., **18**, 3543 (1983).