Formation of SrTiO$_3$ from Sr-oxalate and TiO$_2$

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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.

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

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 Tc-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$_3$

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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: $d_{10}=0.27\mu m$, $d_{50}=0.35\mu m$, $d_{90}=0.48\mu m$) 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 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 40°C for 48 hours.

The decomposition behavior of precursor was characterized using thermogravimetric 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$_\alpha$ 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°, 20 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 350°C, 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:

$$\text{SrC}_2\text{O}_4.\text{xH}_2\text{O} + \text{TiO}_2 = \text{SrC}_2\text{O}_4 + \text{TiO}_2 + \text{xH}_2\text{O}$$

The reaction should produce a theoretical wt. loss of 6.58%, if Sr-oxalate is monohydrate (SrC$_2$O$_4$.1H$_2$O). 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\textsubscript{2}O\textsubscript{4}.1H\textsubscript{2}O and SrC\textsubscript{2}O\textsubscript{4}.2.5H\textsubscript{2}O along with the anatase form of TiO\textsubscript{2}. The excess wt. loss thus suggests that the oxalate hydrate may be a mixture of about 85% SrC\textsubscript{2}O\textsubscript{4}.1H\textsubscript{2}O and 15% SrC\textsubscript{2}O\textsubscript{4}.2.5H\textsubscript{2}O 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].

![DSC/TG tracing of precursor powder](image)

The second stage weight loss (about 10.92%) is due to the formation of SrCO\textsubscript{3} from SrC\textsubscript{2}O\textsubscript{4} as per reactions:

\[
\text{SrC}_2\text{O}_4 + \text{TiO}_2 = \text{SrCO}_3 + \text{CO} + \text{TiO}_2 \\
\text{CO} + \text{O}_2 = \text{CO}_2
\]  

(2) (3)

The theoretical weight loss due to above reactions is 10.09% (for a mixture of 15% SrC\textsubscript{2}O\textsubscript{4}.2.5H\textsubscript{2}O & 85% SrC\textsubscript{2}O\textsubscript{4}.1H\textsubscript{2}O). The experimental weight loss is slightly higher, which may be due to the decomposition of small amount of highly reactive SrCO\textsubscript{3}. Reaction-(2) is an endothermic reaction. A fine endothermic peak at 469°C is corresponding to that carbonate formation reaction. Simultaneously CO is converted exothermically to CO\textsubscript{2} by combining with O\textsubscript{2} from air. The huge exothermic peak followed by the endothermic one is due to the reaction-(3). An XRD analysis of 700°C-DTA samples (Fig. 2) shows the presence of SrCO\textsubscript{3} and TiO\textsubscript{2} only.

The third weight loss, started from about 800°C, is due to the decomposition of SrCO\textsubscript{3} and formation of SrTiO\textsubscript{3}. SrCO\textsubscript{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\textsubscript{3} and simultaneous formation of SrTiO\textsubscript{3}. 

Fig. 1. DSC/TG tracing of precursor powder
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$_2$O$_4$.1H$_2$O (PDF No. 20-1203) and SrC$_2$O$_4$.2.5H$_2$O (PDF No. 20-1204). Only the relative intensity of the peak at 29.42° 2θ or [200] reflection of SrC$_2$O$_4$.1H$_2$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. 2) shows a low intensity [200] peak, comparable to that of the standard. 400°C sample shows, the formation of SrC$_2$O$_4$ 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°C interval in the temperature range 500-900°C, without holding at the peak temperature. No traces of intermediate SrO and/or Sr$_2$TiO$_4$, Sr$_3$Ti$_2$O$_7$ 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°C. Decomposition of carbonate and formation of titanates are rapid from 800°C to 1000°C. The amount of SrCO$_3$ (peak area) decreases rapidly after 800°C. The rapid decomposition of SrCO$_3$ after 800°C may be due to the following two 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°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°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].

![Graph showing non-isothermal transformation kinetics of precursor in static air.](image)
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°C/1hr.

References

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