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Nanosized $SrTiO_3$ powder from oxalate precursor microwave aided synthesis and thermal characterization

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Abstract Nanosized strontium titanate ($SrTiO_3$) was synthesized from strontium titanyl oxalate hydrate, $SrTiO(C_20_4)_2$ $4H_20$ (STO) precursor employing microwave heating technique. STO precursor was characterized by Thermogravimetry (TG) and differential thermal analysis (DTA) techniques prior to the heat treatment in conventional and microwave heating system. STO precursor heated in microwave heating system in air at 773 K for 30 min yielded pure cubic $SrTiO_3$. The product obtained by heating of STO precursor in the same system at 973 K for same duration was, however, much more crystalline. Experiments repeated in conventional furnace showed that $SrTiO_3$ was formed above 973 K. $SrTiO_3$ powder obtained was characterized by X-ray diffraction (XRD) and Transmission electron microscopy (TEM) techniques. TEM study shows that the particles of $SrTiO_3$ are nearly spherical in shape and the particle size of $SrTiO_3$ powder varies between 28 and 68 nm.

Keywords $SrTiO_3$ · Photocatalyst · Microwave heating · Electronic material · Perovskite

Introduction

Strontium titanate ($SrTiO_3$) is a compound with perovskite structure, with a face-centred cubic symmetry [1] and stable over a wide temperature range between 104 and 2300 K [2]. Owing to its high dielectric permittivity and its low microwave losses, it is the most attractive material for many high frequency and microwave applications [3]. This material has been demonstrated to use as a high temperature oxygen sensor [4]. $SrTiO_3$ is one of the promising photocatalyst [5] material used in environmental applications.

Various methods of synthesis of $SrTiO_3$ are reported in the literature. These include conventional ceramic method, sol–gel process, chemical co-precipitation, combustion method, etc. All these methods require very high temperature and prolonged heating period to get a desired product. Now a days microwave heating method is used as alternative low temperature synthesis method [6–8]. In our laboratory we have synthesized mixed oxides at low temperature employing microwave heating technique [9–12]. The compounds synthesized at low temperature have certain advantages like high surface area, small particle size, good sinterability and they are more reactive. This article reports the microwave-assisted low temperature synthesis of nanosized $SrTiO_3$ powder from $SrTiO(C_20_4)_2$ $4H_20$ (STO) precursor.

Experimental procedure

Synthesis of STO precursor

STO used in this study was synthesized from the aqueous solution of strontium nitrate (SN) and potassium titanium oxalate (PTO). SN and PTO used for synthesis were procured from Loba Chemie Pvt. Ltd., Tarapur, India. The method consisted of mixing equimolar aqueous solutions of SN and PTO with constant stirring. The white precipitate obtained was filtered, washed with distilled water and dried in an oven at 313 K for 24 h. The white residue obtained

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was analysed and assigned the molecular formula $\mathrm{SrTiO(C_20_4)_24H_20}$.

Thermogravimetry (TG) and differential thermal analysis (DTA)

TG curve of STO was recorded in flowing argon at the heating rate 10 K $\mathrm{min^{-1}}$ employing simultaneous recording TG/DSC Setaram System (Model 92.16). In addition, DTA plot for thermal decomposition of STO precursor was recorded in flowing air at heating rate 10 K $\mathrm{min^{-1}}$ using the instrument supplied by Universal Thermal Analysis Instruments, Mumbai, India. For recording the DTA plot alumina is used as a reference material.

Preparation of $\mathrm{SrTiO_3}$

$\mathrm{SrTiO_3}$ was prepared by heating STO in a microwave heating system as well as in conventional furnace. The STO precursor was heated at different temperatures from 773 to 973 K (with an interval of 100 K for 30 min) employing the microwave heating system fabricated indigenously. The details of microwave heating system used in this study are described elsewhere [9, 10]. The multimode microwave system used in this study is identical to that described by Roy et al. [13].

Also STO was heated in conventional furnace in a temperature range 773–973 K with an interval of 100 K for 1 h. The products obtained after heat treatment of reactant at different temperatures were analysed by X-ray diffraction (XRD) technique using PANalytical X-ray diffractometer (Model-X'pert Pro MRD), using monochromatic X-ray beam of wavelength 0.15405 nm.

TEM image of $\mathrm{SrTiO_3}$ powder prepared in the present work was recorded using Philips Transmission Electron Microscope (Model CM200). To record TEM image, $\mathrm{SrTiO_3}$ powder was dispersed in isopropyl alcohol and solution was sonicated for 15 min. TEM sample was prepared by drying solvent dispersion of the nanoparticles onto carbon backed Cu grid.

Results and discussion

TG and DTA of STO

TG curve of STO recorded in flowing argon at a heating rate 10 K $\mathrm{min^{-1}}$ is shown in Fig. 1. TG curve shows that STO decomposes in four steps involving dehydration and decarboxylation give $\mathrm{SrTiO_3}$ as the final product above 875 K. The DTA curve recorded in air (Fig. 2) shows two endothermic peaks followed by exothermic peak and a sequence of two minor endothermic peaks. The endothermic peak in DTA curve located ~400 K could be attributed to dehydration of four water molecules represented by reaction (1). An endothermic peak in the temperature range 550–650 K is followed by exothermic peak ~675 K, which could have resulted due to decomposition of carboxylate and simultaneous oxidation of CO evolved in reaction (2). Finally, an endotherm observed above 875 K indicating the formation of $\mathrm{SrTiO_3}$ according to reaction (4). TG and DTA results indicate that thermal decomposition of STO to form $\mathrm{SrTiO_3}$ involves the following sequence of steps.

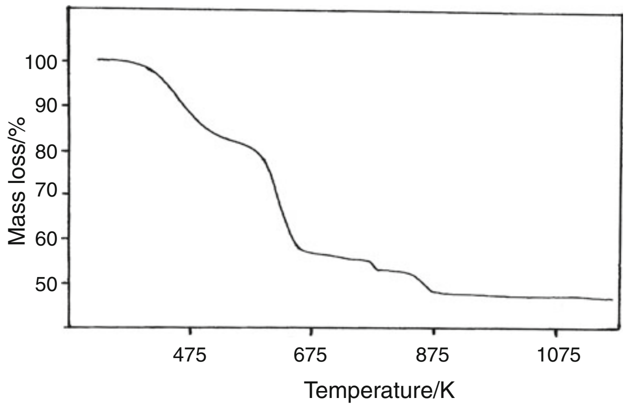


Fig. 1 TG curve of strontium titanyl oxalate (STO) recorded in an argon

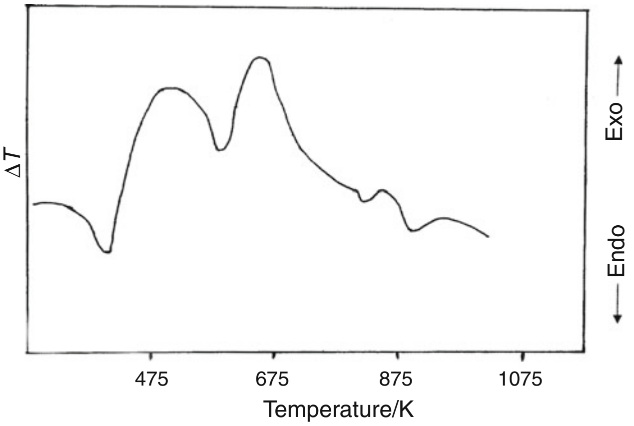


Fig. 2 DTA curve of strontium titanyl oxalate (STO) recorded in flowing air

$$\mathrm{SrTiO(C_2O_4)_2{\cdot}4H_2O \rightarrow SrTiO(C_2O_4)_2+4H_2O} \quad (1)$$

$$\mathrm{2SrTiO(C_2O_4)_2 \rightarrow Sr_2Ti_2O_5(CO_3)(CO_2) + 2CO_2 + 4CO} \quad (2)$$

$$\mathrm{Sr_2Ti_2O_5(CO_3)(CO_2) \rightarrow Sr_2Ti_2O_5(CO_3) + CO_2} \quad (3)$$

$$\mathrm{Sr_2Ti_2O_5(CO_3) \rightarrow 2SrTiO_3 + CO_2} \quad (4)$$

The mass losses expected in each of the above decomposition steps were in good agreement with those calculated

Table 1 TG data as on dried STO precursor

Steps	Temperature range/K	Expected mass loss/%	Observed mass loss/%
I	RT–525	18.02	18.25
II	525–725	25.03	25.48
III	725–825	5.50	4.96
IV	825–1075	5.50	5.22
Total mass loss		54.05	53.91

from the TG curve (Table 1). The steps representing the formation of $SrTiO_3$ from STO concluded from the present studies are identical to those reported by Gopalakrishnamurthy and co-workers[14]. The TG and DTA plots (Fig. 1 and 2) show that thermal decomposition of STO completes above 875 K. This information was used to select the heat treatment temperature for STO precursor to yield $SrTiO_3$.

XRD patterns

The X-ray diffraction patterns of STO calcined in conventional furnace at 773 and 973 K and in microwave heating system at 773 K are shown in Fig. 3. XRD pattern (Fig. 3b) of STO calcined in conventional furnace at 973 K for 1 h showed the formation of pure $SrTiO_3$. This XRD pattern suggests that $SrTiO_3$ formed is cubic in nature and shows good agreement to the JCPD file (PDF No. 401500) of $SrTiO_3$. STO precursor calcined in microwave heating system as low as 773 K for 30 min (Fig. 3c) yielded the same product. The product obtained after calcination of STO precursor in microwave heating system at higher temperature (873 and 973 K) was found to have same structure (cubic) but more crystalline in nature. The XRD pattern of the STO calcined in conventional furnace at 773 K for 1 h (Fig. 3a) shows small amount of $SrTiO_3$ indicating that at this temperature reaction was just initiated. The results indicate that the temperature of synthesis of $SrTiO_3$ is lowered considerably by employing microwave heating.

In the early years of research based on microwave processing of materials, it was assumed that the heating in microwave field was mainly dictated by the dielectric properties of the reactants. The materials with high dielectric loss (tanδ) interacted strongly with the microwave and facilitated rapid heating. In recent years, from the experiments performed in single-mode microwave unit, it is proposed that both dielectric and magnetic properties of materials are involved in the interaction with the microwaves [8, 13, 15]. It has been observed in some cases that the materials which interact much strongly with magnetic field component showed poor interaction with the dielectric component of microwave field.

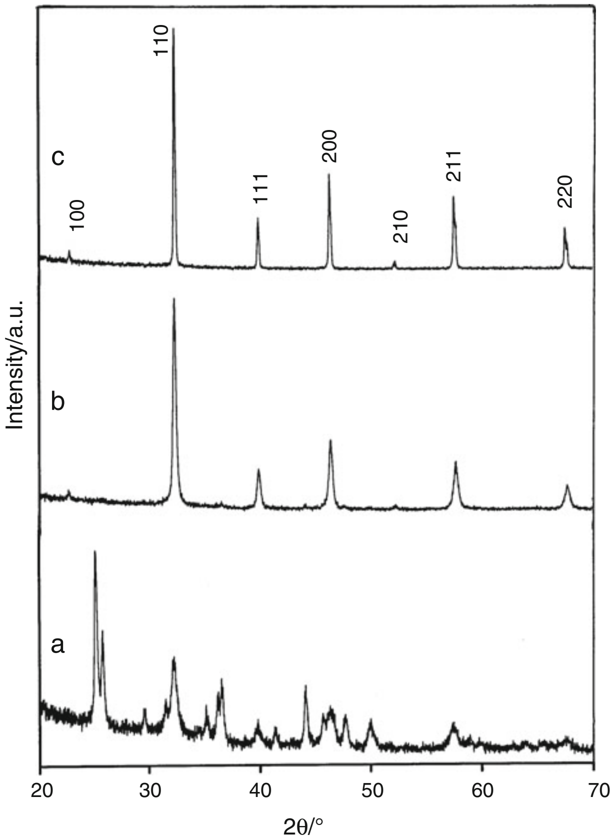
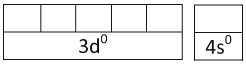
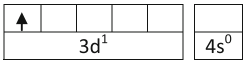
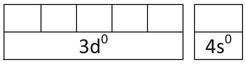
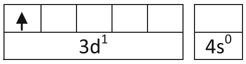
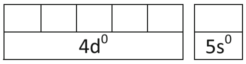
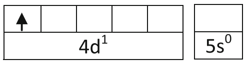
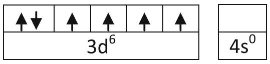
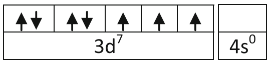
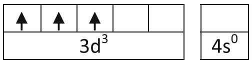
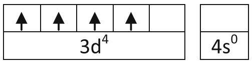


Fig. 3 XRD patterns of strontium titanyl oxalate (STO) calcined at various temperatures **a** 773 K and **b** 973 K in conventional furnace for 1 h, **c** 773 K in microwave heating system for 30 min

In our laboratory we have synthesized various compounds employing microwave heating technique, and the data obtained are presented in Table 2. The critical evaluation of the data presented for the solid state synthesis of $SrTiO_3$, $BaTiO_3$, $LaCoO_3$, $LaCrO_3$ and calcia stabilized zirconia (CSZ) indicates that all these compounds have at least one transition element. All these elements have either one or more unpaired electrons in their d orbitals. It can be seen from this table that in the case of reduced form of Ti(III) and Zr(III), there is a single electron in d orbital. Where as in the case of Co(III) and Cr(III) there are four and three unpaired electrons, respectively, in their d orbitals. In the case of reduced species of these elements, mainly Co(II) and Cr(II), the number of unpaired electrons in Co is three and that in Cr is four.

Formation of $SrTiO_3$, $BaTiO_3$ as well as CSZ in microwave field has been found to take place at much lower temperature than reported by the earlier investigators. This could be understood on the basis of two factors: (1) dielectric properties of reactant and (2) the magnetic properties.

Table 2 Relative contribution from the dielectric and magnetic properties of the reactants to the enhancement of reaction rate

Compound	Properties	Electronic configuration of participating cations	Synthesis temperature/K	Reference number
$SrTiO_3$	D + M	Ti^{+4} Ar[$3d^0$ s^0]  	773	Present work
		Ti^{+3} Ar[$3d^1$ $4s^0$] 		
$BaTiO_3$	D + M	Ti^{+4} Ar[$3d^0$ $4s^0$] 	773	9
		Ti^{+3} Ar[$3d^1$ $4s^0$] 		
$Ca_{0.15}Zr_{0.85}O_{1.85}$	D + M	Zr^{+4} Kr[$4d^0$ $5s^0$] 	673	10
		Zr^{+3} Kr[$4d^1$ $5s^0$] 		
$LaCoO_3$	M	Co^{+3} Ar[$3d^6$ $4s^0$] 	673	11
		Co^{+2} Ar[$3d^7$ $4s^0$] 		
$LaCrO_3$	M	Cr^{+3} Ar[$3d^3$ $4s^0$] 	773	12
		Cr^{+2} Ar[$3d^4$ $4s^0$] 		

D Dielectric property, *M* magnetic property

The oxygen ion vacancies are created by the partial reduction of Ti in case of $SrTiO_3$ and $BaTiO_3$. However, in CSZ oxygen ion vacancies are created both by substitution of Zr(IV) by Ca(II) and partial reduction of Zr(IV) to Zr(III). The oxygen ion vacancies have been reported [6] to interact strongly with the microwaves and the magnetic properties conferred by the presence of unpaired electron in d orbital of these elements could further enhance the reaction in microwave thereby facilitating the reaction at much lower temperature. It is observed that in case of formation of $LaCoO_3$ in microwave heating the temperature of formation is relatively lower than that required for the formation of $LaCrO_3$ suggesting that the Co as well as Cr could be in their highest oxidation state during the synthesis. This would employ that the Co will have four unpaired electrons and Cr will have only three unpaired electrons. It appears that there is direct correlation between the number of unpaired d electrons and reaction temperature in the case of formation of these two compounds.

In the case of synthesis of $SrTiO_3$, $BaTiO_3$ and CSZ, the assumption was made that Ti as well as Zr exist in their reduced state during the synthesis because of the presence of evolved CO. Though there is no difficulty in understanding the lowering of reaction temperature in these three cases, in the case of Co and Cr compounds the trend in the reaction temperature shows that both these elements could be in their highest oxidation state during the synthesis of these compounds in the presence of the microwave field. In +3 oxidation state, Co has four unpaired electrons whereas Cr is having only three unpaired electrons in d orbitals. The higher rate of formation and low synthesis temperature in the case of Co compound could be understood in terms of stronger interaction of Co^{+3} with magnetic component of microwaves compared to that of Cr^{+3}. Since the synthesis of both these compounds is carried out from the oxalate precursors it is necessary to prove that the partial pressure of CO evolved is not high enough to reduce these elements in their lower oxidation state (II) during the time of reaction. It is, therefore, necessary to synthesize these two compounds using other precursors like hydroxides, which will not evolve any reducing gas during the decomposition.

In present case lowering of reaction temperature in microwave system is may be due to two independent factors. In the decomposition of STO, carbon monoxide is evolved which could provide reducing atmosphere in the vicinity of the sample, to yield hypostoichiometric TiO_2 that interacts strongly with microwave, facilitating the reaction at much lower temperature, and the unpaired d electron in reduced titanium ion, i.e., Ti^{3+}, could facilitate the stronger interaction with the magnetic component of the microwave by increasing the reaction rate and lowering the reaction temperature.

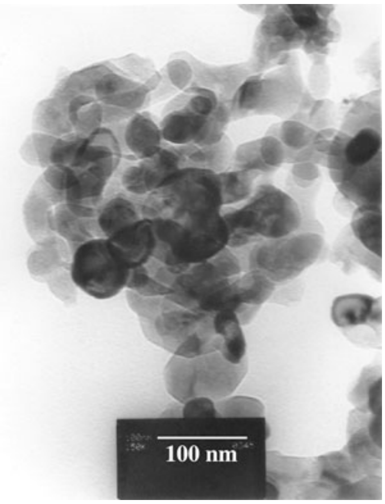


Fig. 4 TEM image of $SrTiO_3$ powder prepared at 773 K employing microwave heating

TEM study of $SrTiO_3$

TEM image of $SrTiO_3$ powder prepared at 773 K employing microwave heating is presented in Fig. 4. This figure shows that the $SrTiO_3$ particles are polydispersed, nearly spherical in shape, and average particle size varies between 28 and 68 nm.

Conclusions

The result obtained in this article shows that nanosized $SrTiO_3$ could be synthesized at low temperature from the oxalate precursor employing microwave heating technique. STO precursor in combination with microwave technique yielded pure cubic nanosized $SrTiO_3$ at temperature as low as 773 K within 30 min. From these, it could be concluded that the microwave heating technique yields $SrTiO_3$ at low temperature within short period; therefore, the particle size of the $SrTiO_3$ formed is very small (28–68 nm).

It can also be concluded from this study that the microwave heating technique is superior compared to the conventional heating technique and yields the product at lower temperature and duration than the conventional process.

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