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Synthesis of $CaTiO_3$ from calcium titanyl oxalate hexahydrate (CTO) as precursor employing microwave heating technique

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Abstract. **Calcium titanate, $CaTiO_3$, an important microwave dielectric material and one of major phases in synroc (synthetic rock), a titanate ceramic with potential application for fixation of high level nuclear waste was synthesized from calcium titanyl oxalate [$CaTiO(C_2O_4)_2 \cdot 6H_2O$] (CTO) by employing microwave heating technique. CTO heated in microwave heating system in air at 500°C for 1 h gave a perovskite, $CaTiO_3$. The product obtained by heating of CTO in the same system at 700°C for the same duration was however, much more crystalline. $CaTiO_3$ obtained by the present method was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and BET surface area measurement.**

Keywords. **Ceramics; synroc; perovskites; electronic materials; microwave synthesis; $CaTiO_3$.**

1. Introduction

Calcium titanate, $CaTiO_3$, with perovskite structure is one of the major phases in Synroc (synthetic rock), a titanate ceramic used for immobilization of high-level nuclear waste (Ringwood *et al* 1979, 1988). It is the major host matrix for strontium, an important radwaste element and can also incorporate significant amounts of lanthanides and actinides (Hanajiri *et al* 1997, 1998). In addition to these nuclear applications, it also finds applications in several electronic devices operating at microwave frequency by virtue of its excellent dielectric properties (Kim *et al* 1999; Suvorov *et al* 2000, 2001; Huang *et al* 2001).

Various methods have been reported in the literature for the synthesis of $CaTiO_3$. These include (i) conventional ceramic technique (Kay and Bailey 1957; Redfern 1996), (ii) organometallic (Yang *et al* 1985), (iii) liquid mix method (Balchandran *et al* 1982; Pan *et al* 2003), (iv) chemical co-precipitation method (Gopalakrishnamurty *et al* 1975), (v) combustion method (Muthuraman and Patil 1994) and (vi) organic–inorganic solution technique (Lee *et al* 2004). Among these methods, the conventional ceramic technique requires high temperatures (>1200°C) and prolonged heating of the reaction components to get the product (Kay and Bailey 1957; Redfern 1996). In other methods, the reaction components are generated *in situ* and are more reactive. Moreover, the particle–to–particle contact in these cases is also more intimate, facilitating the reaction at much lower temperatures. Several other methods involving the mechanical activation of the reactants have also been proposed to reduce the temperature of the reaction (Mi *et al* 1998, 1999; Evans *et al* 2003; Vukotic *et al* 2004).

In the present paper, we have attempted to synthesize $CaTiO_3$ from calcium titanyl oxalate (CTO) by heating it in a microwave heating system as well as in a silicon carbide furnace. The product obtained was characterized by X-ray diffraction (XRD), SEM and BET surface area measurement.

2. Experimental

2.1 *Synthesis of calcium titanyl oxalate (CTO)*

CTO used in the present study was synthesized by chemical co-precipitation method. All the chemicals used were of AnalaR grade. In this method, $CaCO_3$ was dissolved in equimolar aqueous solution of $TiOCl_2$ with constant stirring. This mixture was added to aqueous solution of oxalic acid to maintain the mole ratio Ca : Ti : oxalic acid as 1 : 1 : 2. The aqueous solution was kept over sodium hydroxide pellet in a desiccator for 4 to 5 days when a white precipitate was obtained. The precipitate was filtered through Buckner funnel, washed thoroughly first with distilled water and then with acetone and dried in air. Based on chemical analysis, the product could be assigned the molecular formula, $CaTiO(C_2O_4)_2 \cdot 6H_2O$. The X-ray diffraction pattern recorded for the product showed that it was amorphous and also no lines of calcium oxalate and titanyl oxalate were visible.

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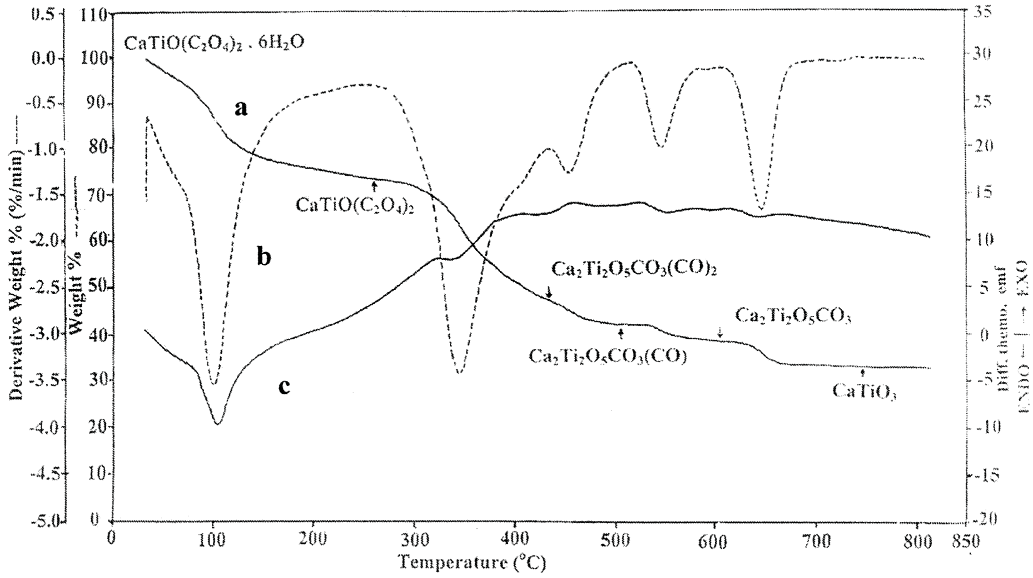

Figure 1. Simultaneous a. TG, b. DTG and c. DTA of calcium titanyl oxalate (CTO) in flowing nitrogen.

2.2 *Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) of CTO*

The simultaneous TG–DTG–DTA curves of CTO were recorded on 2·380 mg of sample in nitrogen at a heating rate of 10°C min^{-1} using the DIAMOND TG-DTA (Perkin Elmer, Germany) Instrument.

2.3 *Preparation of calcium titanate ($CaTiO_3$)*

Calcium titanate was prepared by heating CTO in a microwave heating system as well as in a silicon carbide furnace. CTO was heated in a microwave heating system at temperatures of 500°C and 700°C for 1 h. Also CTO was heated in a silicon carbide furnace at 500°C and 700°C for the same period. The product obtained after heat treatment at different temperatures was analysed by X-ray diffraction using X-PERT X-ray diffractometer, Phillips, at a scanning rate of $1°2\theta\,min^{-1}$, using monochromatic X-ray beam of wavelength, 0·15405 nm.

3. Results and discussion

3.1 *Thermogravimetry (TG), derivative thermogravimetry (DTG) and differential thermal analysis (DTA) of CTO*

The TG, DTG and DTA curves of CTO recorded in nitrogen at a heating rate of 10°C/min are shown in figures 1a, b and c, respectively. These data indicate that CTO decomposes in five steps involving dehydration, decarboxylation to intermediate carbonate and decomposition carbonates to give $CaTiO_3$ as the final product above 650°C. The endothermic peak in DTA curve located around 105°C could be attributed to dehydration of six water molecules to form anhydrous CTO represented by (1). An endothermic peak in the temperature range 300–400°C is followed by two weak exothermic peaks observed in the range 400–600°C, which could have resulted due to decomposition of carboxylate and simultaneous oxidation of evolved CO [(2), (3) and (4)]. Finally, an endotherm is observed at 650°C indicating the formation of $CaTiO_3$ phase according to (5). TG, DTG and DTA indicate that the thermal decomposition of CTO to form $CaTiO_3$ in nitrogen atmosphere involves the following sequence of steps.

$$CaTiO(C_2O_4)_2 \cdot 6H_2O \rightarrow CaTiO(C_2O_4)_2 + 6H_2O, \tag{1}$$

$$2CaTiO(C_2O_4)_2 \rightarrow Ca_2Ti_2O_5CO_3(CO)_2 + 3CO_2 + 2CO, \tag{2}$$

$$Ca_2Ti_2O_5CO_3(CO)_2 \rightarrow Ca_2Ti_2O_5CO_3(CO) + CO, \tag{3}$$

$$Ca_2Ti_2O_5CO_3(CO) \rightarrow Ca_2Ti_2O_5CO_3 + CO, \tag{4}$$

$$Ca_2Ti_2O_5(CO_3)_2 \rightarrow 2CaTiO_3 + CO_2. \tag{5}$$

The five steps involved in the decomposition scheme presented here are based on the stoichiometry of the reaction steps deduced from the mass changes observed in TG. However, the proposed decomposition scheme needs independent support from other complementary techniques like evolved gas analysis. Simultaneous TG–MS studies are in progress to resolve this issue. From the TG and DTA curves it was concluded that the formation of $CaTiO_3$ from CTO precursor was complete above 650°C. It is interesting to note that in the second and third steps of

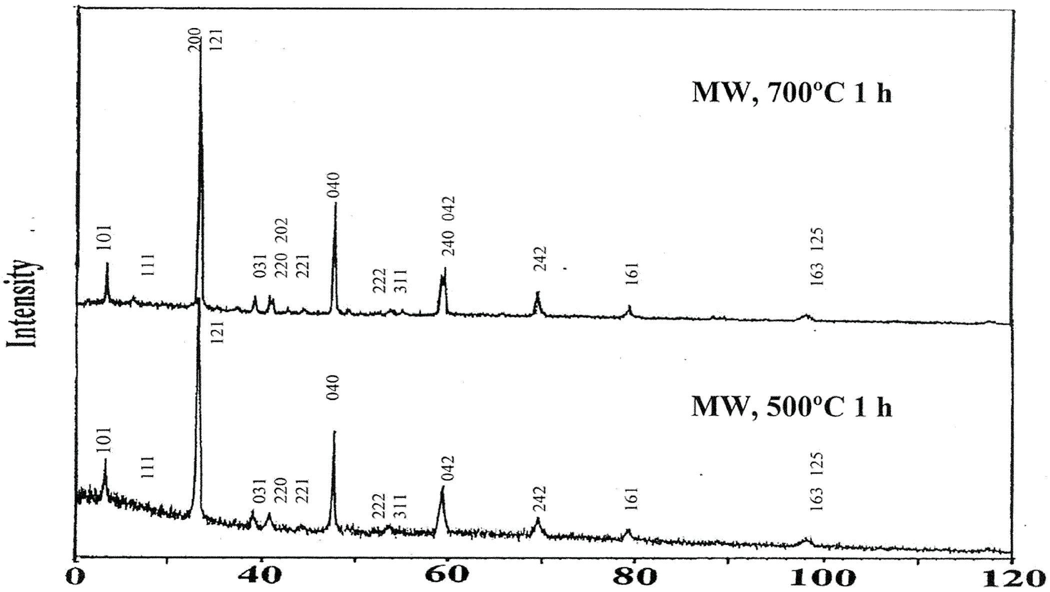

Figure 2. XRD pattern of CTO heated in microwave heating system at a. 500°C and b. 700°C for 1 h.

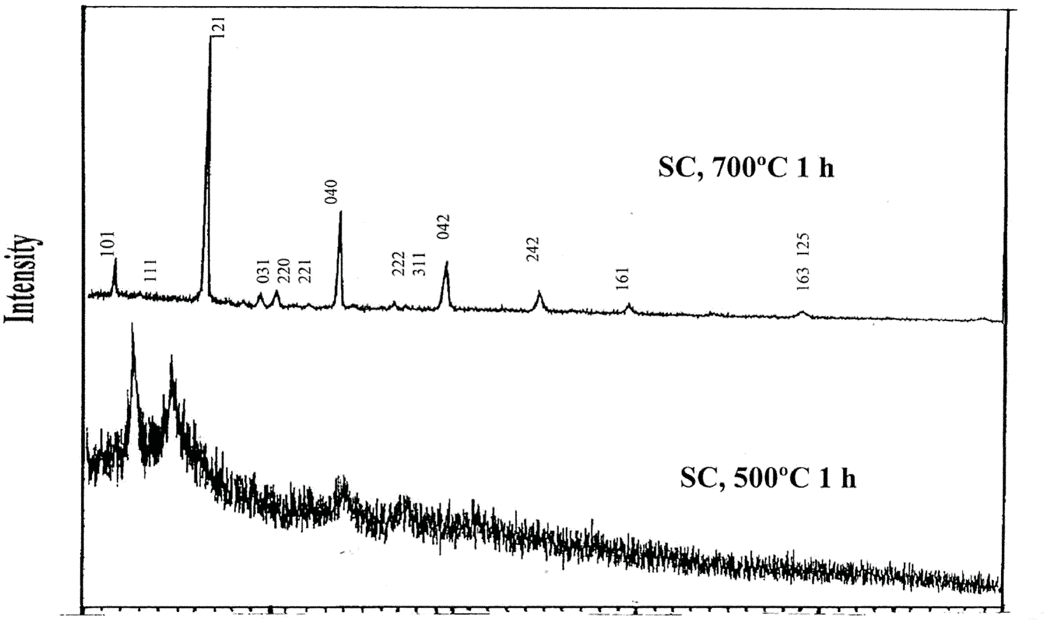

Figure 3. XRD pattern of CTO heated in silicon carbide furnace at a. 500°C and b. 700°C for 1 h.

decomposition of CTO, carbon monoxide is evolved as the gaseous product, which could provide reducing atmosphere in the vicinity of the sample, thereby reducing Ti^{4+} partially to Ti^{3+} which interacts strongly with microwave (Agrawal 1998; Malghe *et al* 2004).

3.2 *X-ray diffraction patterns*

The X-ray diffraction patterns of CTO calcined in microwave heating system at temperatures 500°C and 700°C, for 1 h are shown in figures 2a and b. The corresponding patterns of the product obtained by heating CTO in silicon carbide furnace at 500°C and 700°C for the same duration are shown in figures 3a and b. The CTO calcined in microwave heating system at a temperature as low as 500°C for 1 h (figure 2a) showed the formation of pure perovskite, $CaTiO_3$. The product obtained by heating the same precursor at 700°C in microwave heating system for 1h was found to be much more crystalline compared to that obtained at 500°C. However, calcination of CTO in silicon carbide furnace at 500°C for 1 h could not form the product, $CaTiO_3$, as shown in figure 3a. This is also corroborated from the TG curve (figure 1a), which indicates that the reaction involving the formation of $CaTiO_3$ is not completed at this temperature. The calcination of CTO in silicon carbide furnace at 700°C for 1h was found to yield $CaTiO_3$ which was as crystalline as the product obtained by microwave heating at 500°C for the same duration (figure 3b). The results indicate that the temperature of synthesis of $CaTiO_3$ is lowered considerably by employing microwave heating.

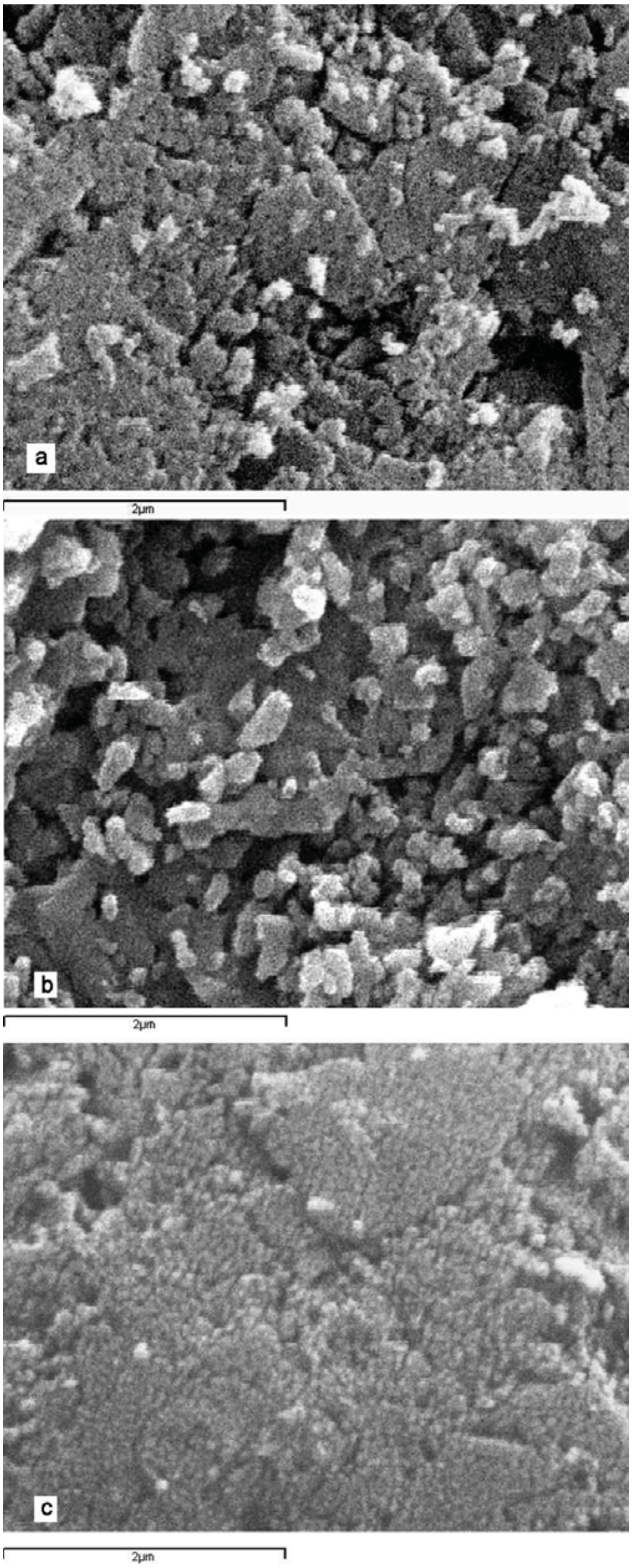

Figure 4. SEM photographs of $CaTiO_3$: **a**. MW, 500°C 1 h, **b**. MW, 700°C 1 h and **c**. silicon carbide furnace, 700°C 1 h.

The results presented in the foregoing sections indicate that perovskite, $CaTiO_3$, could be synthesized by heating CTO at a temperature as low as 500°C. The reducing atmosphere provided by the evolved carbon monoxide [(2) and (3)] could perhaps be responsible to yield non-stoichiometric TiO_2, which subsequently reacted at low temperatures to form $CaTiO_3$.

Our present observations indicate that the lowering of reaction temperature in microwave heating could be the result of two independent factors, which include the interaction of microwave with defects, involving the role of oxygen vacancies and a number of unpaired electrons present in reactants. In the decomposition of CTO, carbon monoxide is evolved as the gaseous product, which could provide reducing atmosphere in the vicinity of the sample, to yield hypostoichiometric TiO_2 that interacts strongly with microwave, facilitating the solid-state reaction at a much lower temperature. Further, the unpaired electrons in reduced Ti ion i.e. in Ti^{3+}, could facilitate stronger interaction with the magnetic component of the microwave thereby augmenting the reaction rate and lowering the reaction temperature (Dharwadkar 2006).

The SEM photographs of $CaTiO_3$ prepared by heating CTO at 500°C and 700°C for 1 h using microwave heating system are shown in figures 4a and b. A similar photograph for $CaTiO_3$ prepared by heating CTO in a silicon carbide furnace at 700°C for 1 h is shown in figure 4c. These photographs indicate that $CaTiO_3$ prepared at 500°C in microwave heating system yields material of very fine particle size. It can be concluded from these figures that an average particle size of the product obtained by microwave heating increased on increasing the temperature from 500–700°C. The product obtained by heating the precursor to 700°C in air, however, had much finer particle size (figure 3c) compared to that obtained at the same temperature by microwave heating (figure 3b), indicating that the fine particle product obtained at low temperature (500°C) by microwave heating sintered much more rapidly with increasing temperature. This is supported by the surface area measurements made by BET

Table 1. Surface area of $CaTiO_3$ prepared by different methods.

Method of heating	Temperature (°C)	Surface area (m^2/g)
Microwave heating	500	11·78
	700	5·56
Silicon carbide furnace	700	8·65

gas adsorption technique. The values of surface area listed in table 1, indicate that the surface area of the product obtained by heating the precursor to 700°C in air is higher than that obtained at the same temperature for the same time duration in the microwave heating.

4. Conclusions

Synthesis of $CaTiO_3$ reported by earlier investigators (Kay and Bailey 1957; Redfern 1996) required high temperature (>1200°C) and long heating periods (more than 12 h). Muthuraman and Patil (1994) synthesized $CaTiO_3$ at 500°C by combustion method but the product obtained was amorphous and further heat treatment at about 900°C was required for crystallization. We adopted a new method in which crystalline $CaTiO_3$ was synthesized from CTO heated in microwave heating system at 500°C within an hour. These observations indicate that the microwave heating facilitates the formation of $CaTiO_3$ from CTO precursor at much lower temperatures.

Acknowledgements

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