# Green Synthesis of Nano-sized Calcium Titanate CaTiO<sub>3</sub> Using Solid State Mechano-Chemical Solventless Method and its Characterization

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Abstract- Calcium titanate (CaTiO<sub>3</sub>) is used as a thermally sensitive resistance element in one of the important materials of ferroelectric ceramics due to its negative temperature coefficient. It has other wide range of applications as components of capacitors, RAM, SYNROC (used for immobilization of nuclear waste). In the present work, we report the preparation of nano-sized calcium titanate (CaTiO<sub>3</sub>) by using solid state mechano-chemical solventless method, which fulfills the requirements of green chemistry. The starting materials used for this synthesis were CaCO<sub>3</sub> and TiO<sub>2</sub>. They were mixed in equimolar ratio (1:1). The mechanical grinding of the reactant mixture was carried in high energy micronizer ball mill by varying the milling time for 0.5h, 1h, 2h, 4h and 5h resulting the peak intensity decrease for the mixture of CaCO<sub>3</sub> and TiO<sub>2</sub> accompanied by decrease in particle size. The as-synthesized products were characterized by X-ray diffraction (XRD) at different stages of milling. After milling, the mixture was calcined at 800°C for 2 hrs. The XRD patterns confirmed the synthesis of nano-sized material of CaTiO<sub>3</sub> at low temperature with high purity.

Keywords: Anatase, Ball-milling, <mark>Mec</mark>hano-chemical, Micro<mark>niz</mark>er, Titanium dioxide.

# I. INTRODUCTION

Calcium titanate (CaTiO<sub>3</sub>) is the representative member of the class of modern ceramics known as perovskites with general formula ABO<sub>3</sub>. It is ferroelectric with an orthorhombic symmetry at room temperature. At higher temperature around 870K, it exhibits tetragonal structure and at even higher temperature of around 1273K, it is transformed into cubic structure [1].

Due to the unique properties of  $CaTiO_3$ , they have been widely used in dielectric materials [2], [3] as capacitors in electronic circuits [4], in the fabrication of ceramic condensers, high frequency filters, microwave resonators and radioactive waste detectors.  $CaTiO_3$  as Dielectric ceramic materials, have temperature stable resonant frequency due to its negative temperature coefficient, low dielectric loss and high relative permittivity, which are used in microwave dielectric applications as filters and resonators [5, 6]. Calcium titanate is one of the main constituent of synroc (titanate based minerals) that was used to store high level radioactive waste [7]. Due to these distinctive properties and numerous uses, much attention has been given for the synthesis of Calcium titanate [8].

In literature, number of different methods have been described for the synthesis of  $CaTiO_3$  powders. These

include sol-gel [9], hydrothermal and process [10], organic inorganic solution method [11] etc. Most of these methods allow producing materials with excellent properties [12]. However, these methods require use of organic solvents and are complex in preparation. In order to overcome these limitations, new methods have been developed to prepare Calcium titanate. The one method that fulfills the requirements of green chemistry, is the solid state mechano-chemical synthesis. It is a solvent free method.

Mechano-chemical method is the combination of mechanical and chemical process. Mechano-chemical method is fundamentally different from the traditional process of heating, dissolving and stirring chemicals in a solution. Moreover, mechano-chemistry excludes the use of many organic solvents needed in industrial chemical processes, making them environment friendly. In micronizer ball milling method, mechanical energy is transported to the powders in mechanical activators called ball mills used to attain chemical transformations, processing and synthesis of nanoparticles. This is an effective method to reduce sample powders to nanosize particles suitable for spectroscopic techniques. The planar shearing and linear impact due to grinding action lead to preservation of crystal lattice, narrow particle size and minimum contamination. Moreover, Miconizer has an



advantage of being compact, easy to clean, maintenance free bench top size model suitable for both wet and dry grinding method.

In the present work, McCrone micronizing mill was used to perform milling, in which precursor  $CaCO_3$  and  $TiO_2$ powders were used to synthesize calcium titanate (CaTiO<sub>3</sub>) using solvent less method, which justifies the requirements of green chemistry and added advantage to get pure products with almost no sample loss. Samples were grinded by varying milling time from 30 min. to 5h. XRD analysis of samples were done to observe any physico-chemical surface parameter changes. Calcination of non-activated and activated samples were carried at 800°C temperature for 2 hours.

The objective of our work is to understand the effect of milling conditions using micronizer on the synthesis of calcium titanate nanoparticles with high purity at low temperature. Mostly, synthesis of calcium titanate has been reported at very high temperature, e.g. Gralik and coworkers have synthesized CaTiO<sub>3</sub> ceramics with perovskite structure at  $1150^{\circ}C$  [13].

### **II. Experimental details**

The starting materials used for the synthesis of calcium titanate (CaTiO<sub>3</sub>) were CaCO<sub>3</sub> (99% purity, Sigma aldrich) and TiO<sub>2</sub> (99% purity) in powder form. They were mixed in the molar ratio of 1:1 in pestle mortar for 10 minutes. The mixture was then dry milled at ambient temperature in a micronizing mill with corundum grinding cylinders as grinding medium in a 125 ml capacity polypropylene grinding jar having built-in screw capped gasket-less polyethylene closure. The polypropylene jar is filled with well-ordered arrangement of 48 identically cylindrical grinding elements, which grind the sample mixture gently via friction.

The milling was achieved by varying the milling time at five levels for different timings upto 5 h. The grinding times were 0.5h, 1h, 2h, 4h, and 5h. The calcination of the 5h milled CaCO<sub>3</sub>:TiO<sub>2</sub> powder was performed at temperatures of 560° and 800°C for 2 hours at 3°C per minute in a programmable muffle furnace. Heated samples were progressively cooled to room temperature.

The effect of milling and calcination on the phase formation of the sample was investigated by using Miniflex 600 powder X-ray diffractometer equipped with 1.54059Å Cu-K $\alpha$  radiation operated with 40kV at 15mA with scan angle of 3-90°. The data is plotted between intensity and scattering angle 2 $\theta$ . For thermal treatment of the material, muffle furnace has been used.

## **III. Results and Discussion**

In this work, calcium titanate  $(CaTiO_3)$  was prepared by using high energy ball milling, micronizer to produce ultrafine powders of nanometer size, which lead to chemical and physical changes in solids when they come into contact due to mechanical forces. This is called mechano-chemical effect.

It has been observed that microstructural changes and size reduction process of calcium titanate during milling procedure were influenced by number of parameters such as milling time, ratio of precursors, grinding speed or stress, calcination of the milled mixture, to mention a few.

XRD technique has been used to characterize the products formed after variable milling time.

The XRD pattern of  $CaCO_3$  is shown in Fig. 1. Each peak corresponds to a particular lattice plane shown by their respective miller indices. The XRD data showed that  $CaCO_3$  has calcite form with trigonal structure and aragonite form with orthorhombic structure. The crystallite size of  $CaCO_3$  is calculated using Debye-Scherrer equation can be written as:

$$\tau = \frac{\kappa\lambda}{\beta Cos\theta}$$

and was found to be 50.06 nm.

The XRD pattern of TiO<sub>2</sub> is shown in Fig. 2. Each peak corresponds to a particular lattice plane shown by their respective miller indices. The peaks at  $2\theta = 25.3^{\circ}$ ,  $37.9^{\circ}$ , 48.00,  $53.9^{\circ}$ ,  $55.1^{\circ}$ , and  $62.7^{\circ}$  have been indexed to represent the (101), (004), (200), (105), (211) and (204) planes of tetragonal anatase phase. The XRD data showed that TiO<sub>2</sub> has anatase form with tetragonal structure. The crystallite size of TiO<sub>2</sub> was determined by using Debye-Scherrer equation and was found to be 33.93 nm.



Position (2θ) in degr



#### Fig. 2 XRD pattern of Titanium Oxide (TiO<sub>2</sub>)

#### *Effect of milling on the synthesis of CaTiO*<sub>3</sub>:

The XRD patterns of CaCO<sub>3</sub>:TiO<sub>2</sub> mixture before milling is shown in Fig. 3, in which main peaks of CaCO<sub>3</sub> (104) and TiO<sub>2</sub> (101) have high intensities. The XRD patterns of mixture of CaCO<sub>3</sub>:TiO<sub>2</sub> after milling are shown in Fig. 4, for 30 min. (a), 60 min. (b), 2h (c), 4h (d) and 5h (e). The XRD data indicated that no reaction had yet been triggered during the milling process as no peak has been observed for CaTiO<sub>3</sub>.



The decrease in the peak intensities of  $CaCO_3$  (104) and  $TiO_2$  (101) in mixture after milling have been observed, which specifies distortion of its crystal structures. In the first 30 min. of milling, the peak intensity decrease is most intensive for the mixture of  $CaCO_3$  and  $TiO_2$  as shown in Fig. 4 (a) accompanied by decrease in particle size. There is only a slight variation in the intensity of  $TiO_2$  peaks (101) after milling for 60 min., 2h, 4h and 5h respectively. However, appreciable decrease in peak intensity of  $CaCO_3$  (104) peaks can be observed (16494.9 to 956.5 counts) from fig. 3 and 4. The dependence of peak intensities of  $CaCO_3$  as a function of milling time has been shown in Fig.







40 50 60 Position  $(2\theta)$  in degrees

(b)

o

20





Fig. 5 Peak as a function of milling intensities of CaCO<sub>3</sub> time.

The average particle size was calculated by using Debye-Scherrer equation. Fig. 6 shows the variation of calculated crystallite size of CaCO<sub>3</sub> and TiO<sub>2</sub> as a function of milling time. It has been observed that the reduction in particle size is maximum for first 30 min. milled mixture and further milling up to 5h lead to the gradual decrease in particle size from 50.05 to 28.61 for CaCO<sub>3</sub> and 33.93 to 27.45 for TiO<sub>2</sub>. This indicated that milling resulted into change in microstructural parameters of TiO<sub>2</sub> and CaCO<sub>3</sub> and reduction in crystalline size.



Fig. 6 Variation of calculated crystallite size of CaCO<sub>3</sub> and TiO<sub>2</sub> as a function of milling time.



The XRD patterns of 5h milled mixture of  $CaCO_3$ :TiO<sub>2</sub> after calcination at 560°C and 800°C for 2 hrs are shown in Fig.7 (a) and (b).

For the 5h milled mixture calcined at  $560^{\circ}$ C, all the XRD diffraction peaks shown in Fig. 7 (a) are attributed to CaCO<sub>3</sub> and TiO<sub>2</sub> only. No peak correlated to CaTiO<sub>3</sub> has been identified up to this temperature. When the 5h milled mixture was calcined at  $800^{\circ}$ C, the dominant diffraction peaks belonging to CaTiO<sub>3</sub> phase appeared in the XRD pattern as shown in Fig. 7 (b).





Fig. 7 XRD patterns of 5h milled mixture of CaCO<sub>3</sub>:TiO<sub>2</sub> calcined at (a) 560°C and (b) 800°C (c) XRD patterns of without milling mixture of CaCO<sub>3</sub>:TiO<sub>2</sub> at 800°C.

The whole amount of CaCO<sub>3</sub> and TiO<sub>2</sub> have been converted into CaTiO<sub>3</sub>. Thus XRD analysis confirmed the existence of pure CaTiO<sub>3</sub> with perovskite structure is in agreement with JCPDS card no. 75-2099. During milling, surface parameter changes in mixture causes increase in the activity of mixture components resulting acceleration in the reactivity of materials [14]. This lead to the formation of small sized CaTiO<sub>3</sub> at low temperature with high purity as compared to heat treated mixture of CaCO<sub>3</sub>:TiO<sub>2</sub> without milling as shown in Fig. 5 (c) at 800°C. As we can observe from Fig. 5 (c), sample without milling does not undergo complete conversion of CaCO<sub>3</sub>:TiO<sub>2</sub> into CaTiO<sub>3</sub> and peaks for CaCO<sub>3</sub> and TiO<sub>2</sub> can be observed. The crystallite size of CaTiO<sub>3</sub> was calculated by using Debye-Scherrer equation and was found to be 23.51 nm.

(a)



## **IV. Conclusion**

In this work, the green method for the synthesis of nano sized Calcium Titanate (CaTiO<sub>3</sub>) has been discussed. The activation of the mixture containing starting material CaCO<sub>3</sub> and TiO<sub>2</sub> has been performed by micronizer ball milling technique using mechano-chemical solventless method. The XRD analysis showed the variation in the intensity of the peaks and reduction in the particle size after milling. In the first 30 min. of milling, the peak intensity decrease is most intensive in the mixture of CaCO<sub>3</sub>:TiO<sub>2</sub> (16494.9 to 956.5 counts for CaCO<sub>3</sub>) and (11248.8 to 2740 counts for TiO<sub>2</sub>). The reduction in particle size is also maximum for first 30 min. milled mixture and further milling up to 5h lead to the gradual decrease in particle size from 50.05 to 28.61 for CaCO<sub>3</sub> and 33.93 to 27.45 for TiO<sub>2</sub>.

The calcination of milled and without milling mixture of  $CaCO_3$  and  $TiO_2$  has been done at 800°C temperature to synthesize CaTiO\_3. The crystallite size of CaTiO\_3 particles was found to be 23.51 nm. In 5h milled mixture, XRD analysis confirmed the formation of nano-sized pure CaTiO\_3 with perovskite structure. Formation of small sized CaTiO\_3 took place at low temperature with high purity as compared to calcined mixture of CaCO\_3:TiO\_2 without milling.

## REFERENCES

- [1] S. Redfern, "J. Phys. Condens. Matter", 1996, Vol. 8, pp. 8267-8275.
- [2] Gmelins Handbook of Inorganic Chemistry, Leipzig, 1951, Vol. 41-42.
- [3] H. Landolt & R. Boernstein, "Values and Functions in Physics, Chemistry, Astronomy, Geophysics and Technology", Springer Verlag, Berlin, 1957, Vol. 4 (3).
- [4] J. M. Herbert, "Ceramic Dielectric and Capacitors", Engine Gordon and Breach, 1985.
- [5] G. Mi, Y. Murakami, D. Shindo, F. Saito "Mechanochemical synthesis of CaTiO3 from a CaO-TiO2 mixture and its HR-TEM observation", Powder Technology, 1999, 105, 162-166.
- [6] X. Lei, B. Xu, B. Yang, B. Xu, and X. Guo, "A novel method of synthesis and microstructural investigation of calcium titanate powders", Journal of Alloys and Compounds, 2017, 690, 916-922.
- [7] D. M. Levins & K.D. Reeve, "American Nuclear Society Int. Meeting on Waste Management", Niagara Falls, NY, 1986.
- [8] G. Pfaff, "Synthesis of calcium titanate powders by the sol-gel process." Chemistry of materials, 1994, 6, 58-62.

- [9] S. J. Lee, Y. C. Kim, and J. H. Hwang. "Organicinorganic solution technique for fabrication of nanosized CaTiO3 powder,"Journal of Ceramic Processing & Research, 2004, 5, 223-226.
- [10] P. T. Anastas, and J. C. Warner. "Principles of green chemistry," Green chemistry: Theory and practice (1998): 29-56.
- [11] T. R. N. Kutty, R. Vivekanandan, and P. Murugaraj.
  "Precipitation of rutile and anatase (TiO2) fine powders and their conversion to MTiO3 (M= Ba, Sr, Ca) by the hydrothermal method" Materials chemistry and physics 1988, 19, 533-546.
- [12] S. Sahoo, U. Dash, S. K. S. Prashar, S.M. Ali, "Frequency and temperature dependent electrical characteristics of CaTiO3 nano-ceramic prepared by high-energy ball milling." Journal of Advanced Ceramics, 2013, 2, 291-300.
- [13] G. Gralik, A. E. Thomsen, C. A. Moraes, F. R. Pereira, D. Hotza, "Processing and characterization of CaTiO3 perovskite ceramics" 2014, 8, 53–57.
- [14] Petrovic, Vera, "Synthesis of calcium-titanate (CaTiO3)."