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Microwave-Assisted Formation of Phase-Pure Rutile TiO2 from Titanium Tartrate Precursor: A Facile Route toward Dense SYNROC Ceramics

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ABSTRACT

Titanium dioxide (TiO2) is an essential ceramic component of SYNROC (synthetic rock), used for immobilizing high-level nuclear waste due to its excellent chemical stability and high density. In the present study, TiO2 was synthesized via a tartrate route using a titanium tartrate (TT) precursor. The synthesis involved oxidation of Ti3+ to Ti4+ in TiCl3 solution with ammonium nitrate, followed by complexation with tartaric acid. The resulting titanium tartrate was dried at 200 °C and subsequently calcined in both muffle and microwave furnaces at different temperatures to obtain TiO2.The thermogravimetric (TG) and differential thermal analysis (DTA) curves revealed a two-step decomposition behaviour, with initial dehydration below 250 °C and major organic decomposition around 550 °C, leading to the formation of TiO2. A broad exothermic peak near 1050 °C corresponded to the anatase-to-rutile phase transformation. X-ray diffraction (XRD) studies confirmed that the as-prepared precursor was amorphous and crystallized into the anatase phase above 500 °C, which transformed partially to rutile at 1000 °C in the muffle furnace. Under microwave heating, crystallization initiated at a lower temperature (≈300 °C) with complete transformation to rutile at 600 °C—about 400 °C lower than in the muffle furnace. FTIR spectroscopy confirmed the disappearance of organic functional groups and the formation of Ti–O bonds with increasing calcination temperature. FE-SEM micrographs revealed nearly spherical nanoparticles (25–40 nm) at lower temperatures, which agglomerated into larger grains at higher temperatures. The anatase-to-rutile transformation was found to enhance densification, leading to sintered TiO2 pellets with nearly 95% of theoretical density when sintered at 1250 °C. The results demonstrate that the tartrate route provides a facile and energy-efficient method for obtaining phase-pure rutile TiO2 suitable for advanced ceramic and SYNROC applications.

KEYWORDS: Titanium dioxide (TiO2); Tartrate precursor; Anatase–rutile transformation; Microwave synthesis

INTRODUCTION

Titanium dioxide (TiO_2) is one of the major components of SYNROC (synthetic rock), a durable ceramic material designed for immobilizing high-level nuclear waste [1]-[4]. TiO_2 exists in three distinct polymorphic forms: brookite, anatase, and rutile. Among these, brookite possesses an orthorhombic structure and is relatively uncommon. Anatase crystallizes in a metastable tetragonal form, which transforms spontaneously into another tetragonal modification, rutile, the thermodynamically most stable phase of TiO_2. Structurally, anatase consists of a three-dimensional framework formed by corner-sharing TiO_6 octahedra, whereas in rutile, the structure evolves through edge-sharing of TiO_6 octahedra. The molar volume of rutile (18.693 cm^3mol^{-1}) is smaller than that of anatase (20.156 cm^3 mol^{-1}), indicating its denser and more stable configuration [5].

TiO_2 constitutes approximately 70% of the total oxides involved in the formation of various SYNROC phases [3], [4], [6], [7]. Consequently, the phase transformations of TiO_2 play a crucial role in determining the formation and stability of SYNROC phases. The anatase-to-rutile transformation in TiO_2 has been extensively studied [8]. This transformation, involving the conversion from metastable anatase to stable rutile, is strongly influenced by several factors such as the presence of impurities, specific surface area, particle size, and the thermal treatment conditions of the precursor material.

Due to its metastable nature, the transition temperature from anatase to rutile varies significantly depending

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on factors like impurity content, synthesis method, and precursor characteristics. Therefore, in the present study, it was considered essential to investigate the structural characteristics of TiO_2 synthesized via the thermal decomposition of a tartrate precursor, and to evaluate how these characteristics influence the densification behavior during the sintering of SYNROC.

MATERIALS AND METHODS:

All the chemicals employed were of AnalaR grade, 15% $TiCl_3$ and Tartaric acid and Ammonium nitrate from S. D. Fine Ltd., Mumbai.

1.1. Synthesis of TiO_2 nanoparticles:

In this process, 100 cm^3 of 0.2 M ammonium nitrate solution was added to 100 cm^3 of 0.2 M $TiCl_3$ solution. The addition of NH_4NO_3 to $TiCl_3$ caused an exothermic oxidation of Ti^{3+} to Ti^{4+} in the solution, accompanied by a colour change from violet to pale green. Subsequently, 100 cm^3 of 0.4 M tartaric acid solution was added to this mixture with constant stirring [9]. The resulting solution was then heated in an air oven at 200°C until complete dryness. A free-flowing brown-coloured titanium tartrate precursor powder was obtained, which, upon thermal decomposition at elevated temperatures, yielded pure TiO_2. The heating of the tartrate precursor powder was carried out in both a muffle furnace and a microwave oven

1.2. Characterization

The simultaneous TG–DTA analysis of the titanium tartrate precursor was carried out in flowing air using a DIAMOND TG–DTA instrument (Perkin Elmer, Germany). The TiO_2 powders obtained after heat treatment at various temperatures were characterized by X-ray diffraction (XRD) using a Rigaku Miniflex II diffractometer with a monochromatic Cu Kα radiation source (λ = 0.15405 nm). The morphology of the TiO_2 nanoparticles was examined by field emission scanning electron microscopy (FE-SEM, JEOL JSM-7600F) and high-resolution transmission electron microscopy (HR-TEM, FEI Tecnai G2 F30, 300 kV).

The synthesized TiO_2 powder was pelletized at a pressure of 50 MPa into discs of 8 mm diameter and 5 mm thickness, and subsequently sintered in air at 1250 °C with a heating rate of 10 °C min^{-1} for 5 h. The bulk density of the sintered pellets was determined using the Archimedes liquid displacement method

RESULTS AND DISCUSSION

3.1: The Synthesis of Rutile TiO_2 via Titanium Tartrate (TT) precursor

The flow chart illustrating the synthesis of the titanium tartrate precursor and the subsequent formation of rutile TiO_2 through its thermal decomposition is presented in Figure 1. The synthesis procedure involves the oxidation of Ti^{3+} to Ti^{4+} in a $TiCl_3$ solution by the addition of ammonium nitrate, followed by the introduction of an appropriate stoichiometric amount of tartaric acid. The resulting solution is then evaporated to dryness by heating in an air oven at 200°C, yielding a brown, free-flowing titanium tartrate powder.

The obtained precursor is subsequently calcined in both a muffle furnace and a microwave furnace at different temperatures to produce TiO_2. The phase formation and crystallinity of the synthesized TiO_2 samples were analyzed using X-ray diffraction (XRD) patterns.

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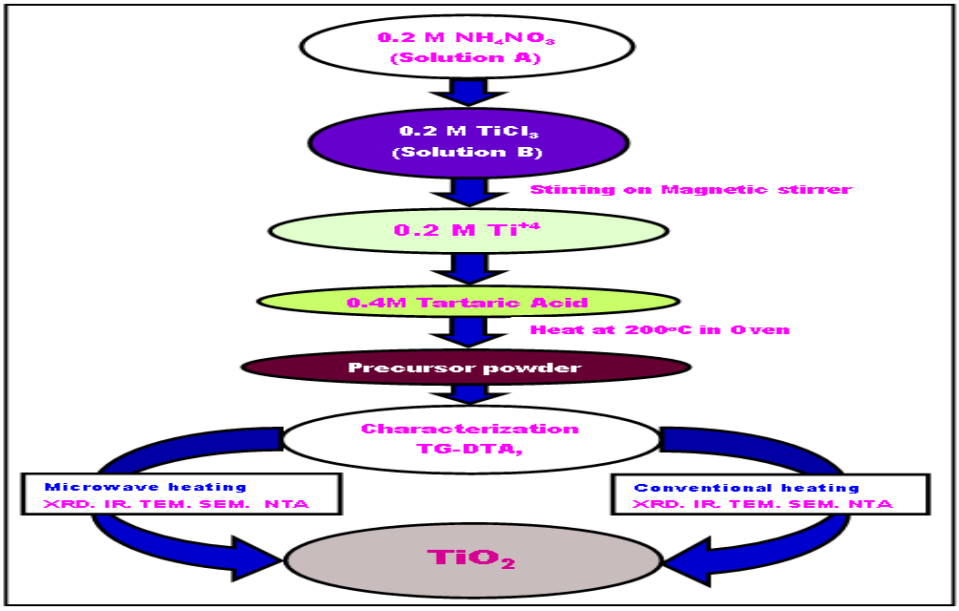

Fig. 1: Flow chart for the synthesis of Rutile TiO_2 from Titanium Tartrate (TT) precursor.

3.2: Thermogravimetry (TG) and Differential Thermal Analysis (DTA) study of Titanium Tartrate (TT) precursor:

The simultaneous thermogravimetric (TG) and differential thermal analysis (DTA) curves recorded for the titanium tartrate precursor in air are presented in Figure 2. The TG curve shows the onset of mass loss from the beginning of the temperature rise, which levels off around 150 °C, forming a plateau between 150 and 250 °C. The mass loss in this region, approximately 5%, can be attributed to the removal of adsorbed or residual water from the precursor.

This is followed by a major weight loss step terminating around 550 °C, which likely corresponds to the thermal decomposition of the tartrate ligand, leading to the formation of TiO_2. Subsequently, a gradual mass gain of about 5% is observed between 550 and 1200 °C, possibly due to the oxidation of hypostoichiometric TiO_{2-x} formed during the decomposition process. The broad exothermic peak observed in the DTA curve may be attributed to the thermal decomposition of titanyl tartrate and the simultaneous oxidation of carbon monoxide (CO) evolved during decomposition. Another exothermic event, initiated around 1050 °C, could be associated with the anatase-to-rutile phase transformation of TiO_2. This transformation near the same temperature is further supported by the XRD pattern of the product obtained by heating the titanium tartrate precursor at 1000 °C (Figure 3e).

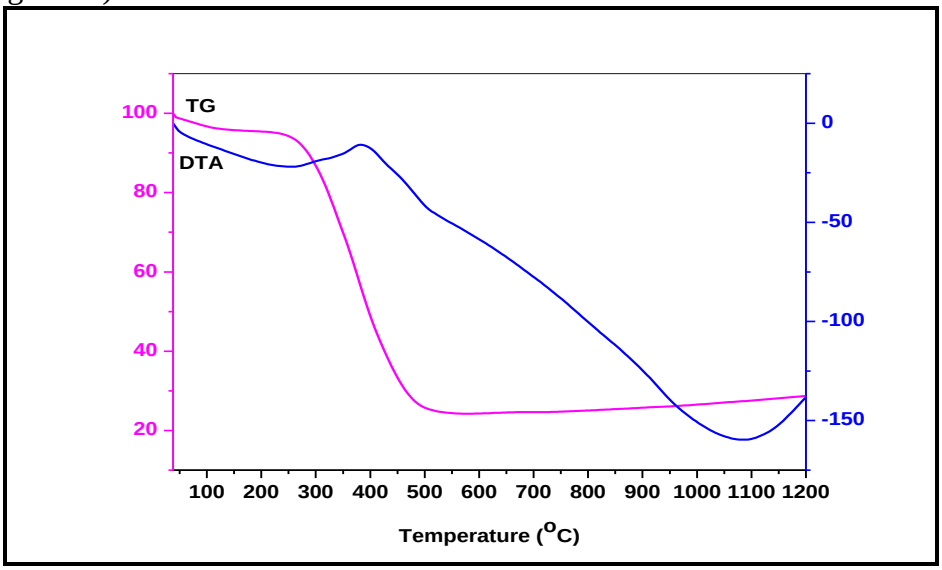

Fig: 2: Simultaneous TG - DTA curve of Titanium tartrate (TT) precursor recorded in air.

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3.3: X-ray Diffraction Study of TiO_2 obtained from TT precursor:

The X-ray diffraction (XRD) patterns of the products obtained by heating the titanium tartrate precursor at different temperatures in a muffle furnace for one hour are presented in Figure 3. The XRD results indicate that the titanyl tartrate precursor, dried at 300 °C, is amorphous, and begins to crystallize into the anatase phase above 500 °C (JCPDS 21-1272) (Figure 3a, b) [10]. It is further observed that a single-phase anatase structure persists up to 900 °C (Figure 3d). The XRD pattern recorded for the precursor heated at 1000 °C in the muffle furnace for one hour shows a partial transformation of the anatase TiO_2 phase into the rutile TiO_2 phase (JCPDS 34-0180) [10].

The XRD patterns of the tartrate precursor heated at various temperatures in a microwave oven for one hour in air are shown in Figure 4. The overall patterns are similar; however, crystallization begins at a lower temperature of around 300 °C, forming the anatase phase (JCPDS 21-1272). Almost complete transformation to rutile (JCPDS 34-0180) is observed at 600 °C (Figure 4e), which is approximately 400 °C lower than the temperature required for the same transformation in the muffle furnace.

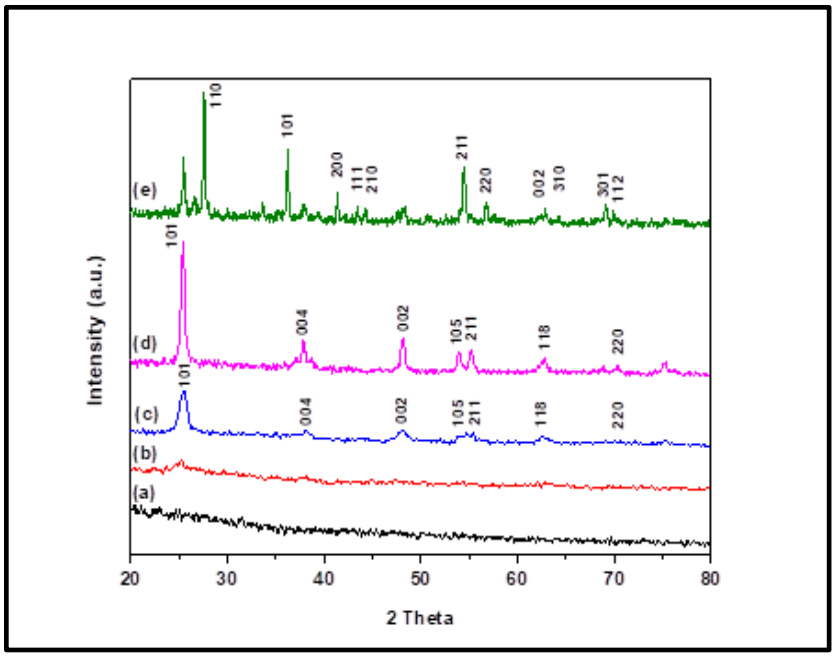

Fig. 3: XRD patterns of TT precursor calcined in Muffle furnace (a) as prepared (b) 500 (c) 700ºC (d) 900ºC (e) 1000ºC for one hour.

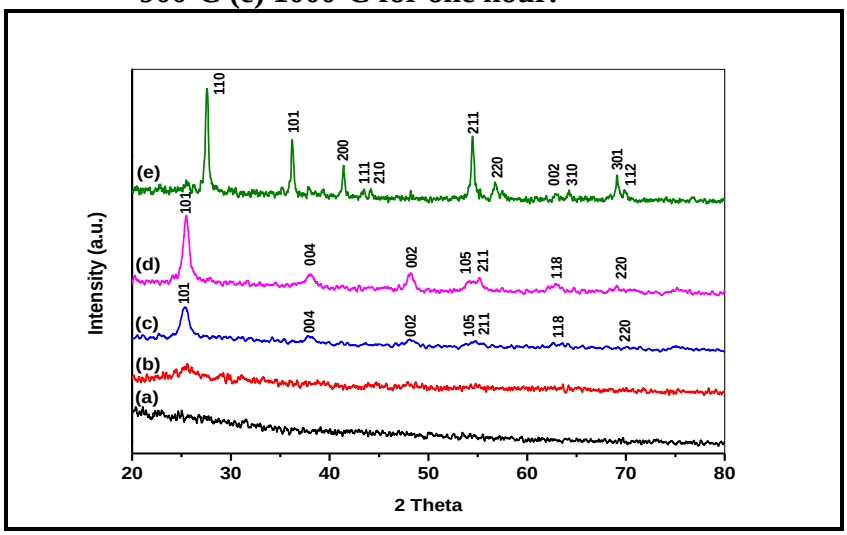

Fig. 4: XRD patterns of TT precursor calcined in Microwave heating system (a) as prepared (b) 300ºC (c) 400ºC (d) 500ºC e) 600ºC for one hour.

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The anatase-to-rutile transformation is accompanied by a decrease in molar volume, which can facilitate densification and sintering in samples containing anatase. Consequently, SYNROC blends containing the anatase phase are expected to sinter more readily than those containing rutile, as the transformation is associated with volume shrinkage. The densities of rutile and anatase TiO_2 are 4.27 g cm^{-3} and 3.90 g cm^{-3}, respectively [5].

3.4: FTIR spectroscopy of the TT precursor calcined at different temperatures in Muffle Furnace:
The FTIR patterns for Tartaric acid, TT precursor and the products obtained by heating it to different temperatures for one hour are presented in Fig. 5. The figure brings out clearly the difference in wave numbers observed for tartaric acid and that for the precursor brought about due to bonding of the former with the metal atom. Most of the wave numbers due to organic moiety observed in the precursor are however seen to be clearly absent in the products obtained by heating the precursor at 900 and 1000^0 C. The FTIR patterns recorded at these temperatures are nearly the same indicating subtle difference in the low wave number region. These peaks could represent the metal-oxygen bonding in the oxides produced by thermal decomposition of the precursor.

The FTIR spectra of the TT precursor (Fig. 5b) show the broad peak near 3434 cm^{-1}, representing the stretching vibrations of O-H group of water. The peak at 1620 cm^{-1} is attributed to bending vibration of O-H group of water and stretching vibrations of C=O group of oxalates/ tartrate. The peak at 2930 indicates the C-H stretching vibration in tartrate. The band observed at 1440 cm^{-1} represents the unidentate nature of the C-O vibration. The bands at 1125 cm^{-1} could correspond to the bending vibration of the C-O of the oxalate moiety. The bands at 822, 641 and 527 cm^{-1} could be assigned to the stretching vibrations of the Ti–O bonds. The intensity of the peak around 1629 decreased with increased annealing temperature indicates the decomposition of intermediate carbonate. At 900ºC, the peak observed at 527cm^{-1} could be assigned to Ti-O bond in Anatase form of TiO_2. The TT precursor heated at 1000ºC for one hour in Muffle furnace, new peaks appeared at 426 cm^{-1} which could be assigned to stretching vibration of Ti-O in Rutile TiO_2 [11]. These observations are collaborating with the TG-DTA and XRD results obtained by heating the TT precursor in Muffle Furnace (Fig. 2 and Fig. 3).

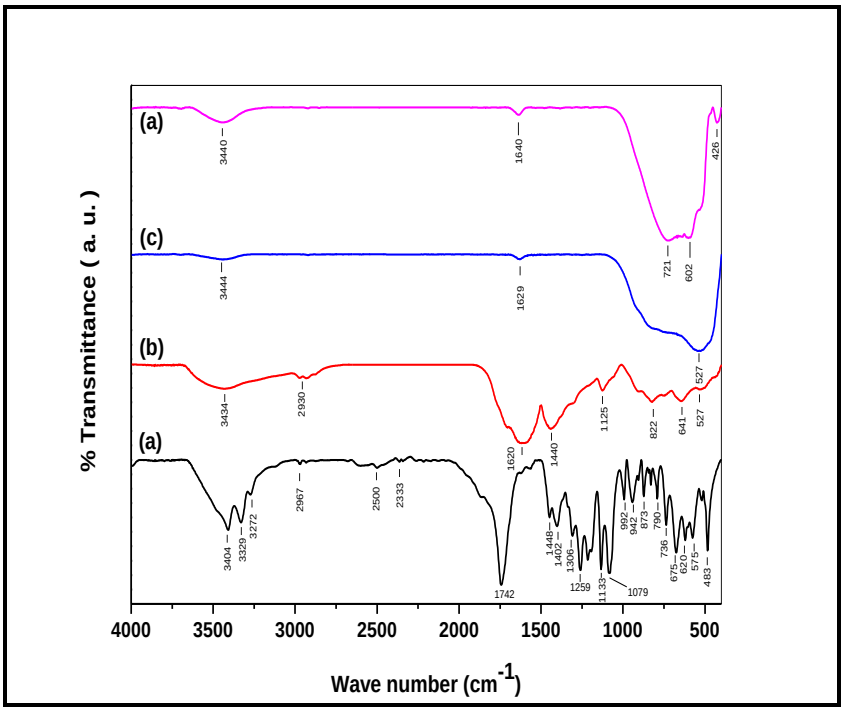

Fig. 5: FTIR spectra (a) L-tartaric acid (b) as prepared Titanium tartrate precursor and TT precursor calcined in Muffle furnace at (c) 900ºC (d) 1000ºC for one hour.

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3.5: Field Emission Scanning Electron study of TiO_2 obtained from TT precursor:

The field-emission scanning electron microscopy (FE-SEM) images of TiO_2 obtained by heating the titanium tartrate precursor at 900 °C and 1000 °C in a muffle furnace under air atmosphere are presented in Figures 6a and 6b, respectively. The micrograph of the sample heated at 900 °C reveals the formation of uniform, nearly spherical nanoparticles with an average particle size in the range of 25–30 nm. Upon heating to 1000 °C, these nanoparticles exhibit agglomeration, resulting in the formation of larger, non-uniform grains with a broad size distribution ranging from 25 nm to 0.35 µm.

Similarly, the FE-SEM images of TiO_2 obtained by heating the precursor at 500 °C and 600 °C in a microwave furnace for one hour in air are shown in Figures 7a and 7b, respectively. The particles produced under microwave heating are also nearly spherical and uniformly distributed. The particle size of the TiO_2 formed at 500 °C in the microwave furnace is comparable to that of the sample synthesized at 900 °C in the muffle furnace. The product obtained at 600 °C exhibits a narrow particle size distribution, with particle diameters in the range of 30–40 nm. The formation of uniformly sized TiO_2 nanoparticles in the SYNROC matrix up to about 900 °C is advantageous for enhanced sintering behavior, as the nanoscale particles promote better packing and compaction of the cold-pressed green bodies derived from the titanium tartrate precursor. Furthermore, the anatase-to-rutile phase transformation observed above 950 °C, accompanied by an increase in density, is expected to further enhance sintering kinetics.

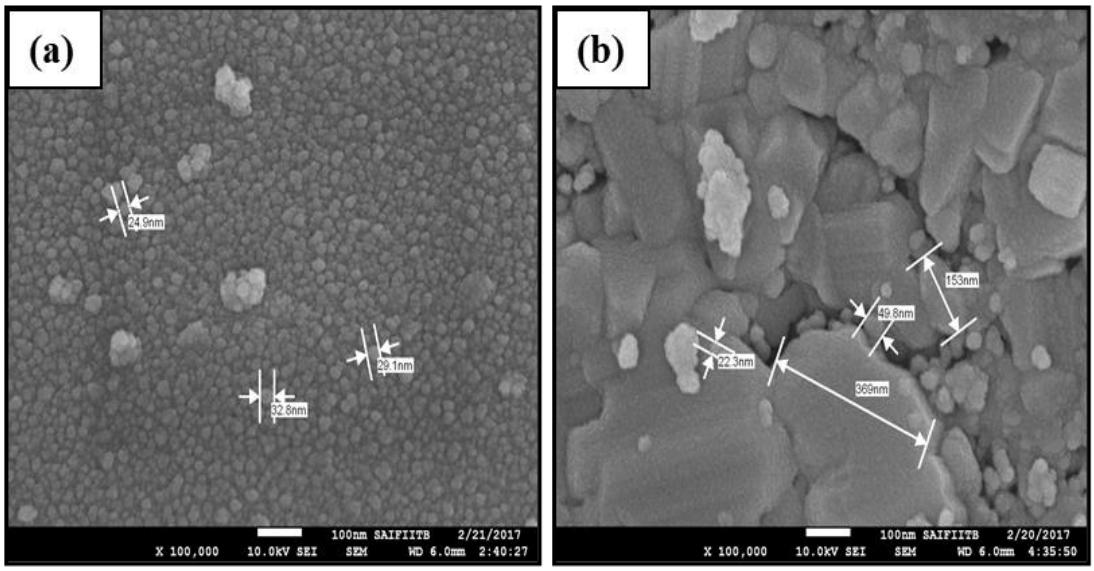

Fig. 6: SEM images of TiO_2 powder obtained from titanium tartrate precursor calcined in Muffle furnace at (a) 900°C (b) 1000°C for one hour.

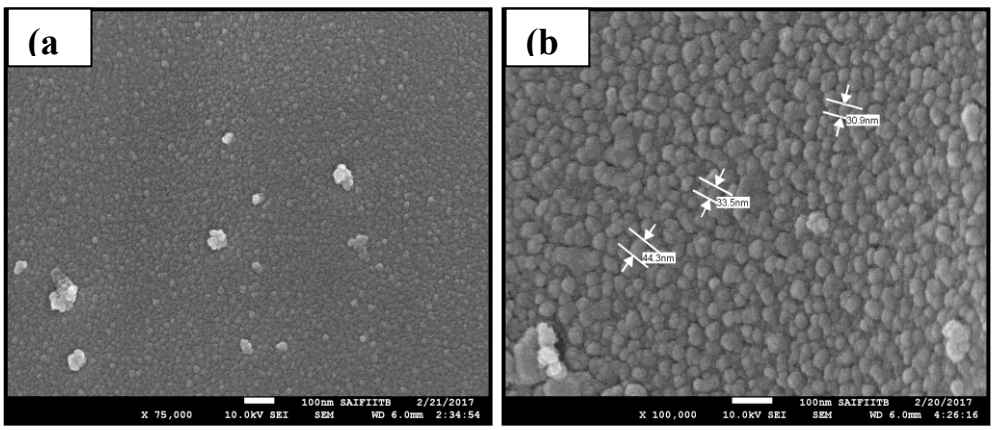

Fig. 7: SEM images of TiO_2 powder obtained from titanium tartrate precursor calcined in Microwave oven at (a) 500°C (b) 600°C for one hour.

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The SEM micrograph of the TiO_2 pellet sintered at 1250 °C is shown in Figure 8. The image reveals a well-developed, densely packed microstructure composed of closely bonded nanocrystals, suggesting that the sintered compact achieved a density close to 95% of the theoretical value, as confirmed by liquid displacement measurements [12].

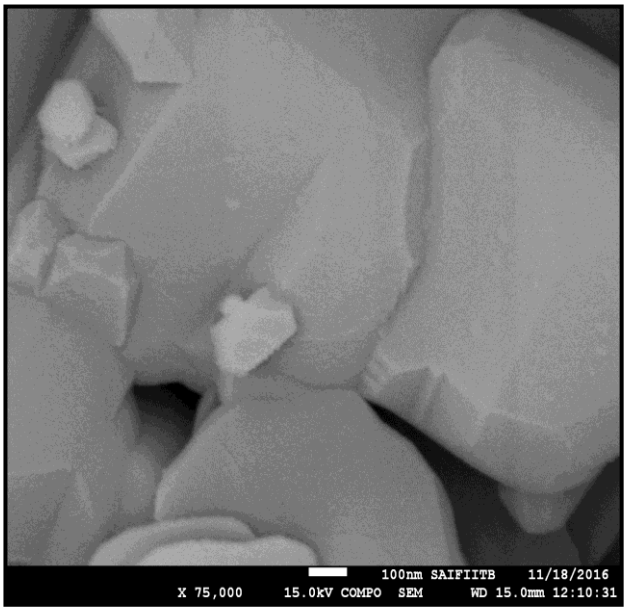

Fig. 8: SEM images of sintered pellet of TiO_2 at 1250°C in muffle furnace

3.6: Density Measurement:

The density of sintered Rutile TiO_2 pellets was determined employing the liquid displacement method. The density of the Rutile TiO_2 pellet sintered at 1250°C for five hours was found to be nearly ~ 95 % of theoretical value.

CONCLUSION

The present investigation demonstrates the successful synthesis of TiO_2 via a tartrate precursor route, providing a simple and effective pathway for producing high-purity rutile TiO_2. The TG–DTA analysis confirmed the stepwise decomposition of titanium tartrate, leading to oxide formation near 550 °C and subsequent phase transformation from anatase to rutile around 1050 °C. XRD results indicated that the titanium tartrate precursor remained amorphous up to 500 °C, crystallized into anatase beyond this temperature, and gradually transformed into rutile at 1000 °C when heated in a muffle furnace. Microwave-assisted synthesis produced comparable results at significantly lower temperatures, confirming its energy efficiency and accelerated kinetics. FTIR spectra provided evidence for the elimination of organic functional groups and the formation of Ti–O bonding upon heating. The FE-SEM analysis revealed nanosized, nearly spherical TiO_2 particles (25–40 nm), which agglomerated at higher calcination temperatures. The fine and uniform microstructure observed below 900 °C promotes effective packing and enhances sintering behaviour. The anatase-to-rutile transformation, associated with an increase in density, further facilitates densification during sintering. The TiO_2 pellet sintered at 1250 °C exhibited a dense microstructure with well-developed nanocrystals and achieved approximately 95% of theoretical density, as verified by liquid displacement measurements. The results collectively confirm that the tartrate route is a viable and energy-efficient synthesis method for obtaining nanocrystalline TiO_2 with desirable structural, morphological, and sintering characteristics, making it a promising approach for SYNROC fabrication and advanced ceramic applications.

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