Periodica Polytechnica Chemical Engineering, 68(4), pp. 582–586, 2024

Preparation of Magnesium Titanate by Using Magnesium Chloride a Byproduct of Titanium Plant

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Received: 08 July 2024, Accepted: 01 October 2024, Published online: 28 October 2024

Abstract

This study explores the preparation of magnesium titanate using magnesium chloride, a byproduct of the titanium production plant as a precursor. The synthesis involves the reaction of $MgCl_2$ with titanium tetrachloride under controlled thermal conditions. Initially, $MgCl_2$ and $TiCl_4$ are thoroughly mixed in stoichiometric proportions with an excess of oxalic acid solution to produce magnesium titanyl oxalate. The mixture is then subjected to a calcination process at temperatures ranging from 300 °C to 1000 °C in an oxygen-rich environment. The physicochemical properties of the synthesized $MgTiO_3$ were analyzed using EDS, XRD, TG/DTA, SEM, and particle size analysis. This comprehensive set of analytical techniques provides a thorough understanding of the elemental, structural, thermal, morphological and physical characteristics of magnesium titanate. The formation of pure magnesium titanate is confirmed at temperatures above 800 °C, with lower temperatures leading to the presence of intermediate phases such as $MgTi_2O_5$. The synthesized $MgTiO_3$ exhibits a homogeneous microstructure with well-defined grain boundaries, indicating successful preparation of the desired ceramic material.

Keywords

magnesium titanate, ceramic materials, synthesis, byproduct utilization, physiochemical characterization

1 Introduction

Magnesium titanate ($MgTiO_3$) is a versatile ceramic material renowned for its excellent dielectric properties, high thermal stability, and chemical inertness, making it valuable for applications in electronics, catalysis, and as a refractory material [1, 2]. Its perovskite crystal structure, where magnesium ions occupy the A-site and titanium ions occupy the B-site, contributes to its robust physical and chemical properties [3].

In previous findings, it was found that magnesium titanate was synthesized using aqueous slurries of $Mg(OH)_2$ and TiO_2 powders by employing a wet milling technique equipped with stabilized zirconia rings. An increase in slurry concentration improves the homogeneity of the product, facilitating the formation of single-phase $MgTiO_3$ after subsequent drying at 50 °C for 24 h [4]. Magnesium-calcium titanate was prepared via semi-alkoxide methods using magnesium and calcium precursors with titanium isopropoxide. The formation of crystallites was observed at 500 °C [5]. By the reaction of an alcoholic solution of titanium *n*-butoxide with nitrate solutions, multiple oxides of titanium (Mg, Ca, Sr, Ba) were prepared by using sol-gel method. High pure magnesium titanate crystallites were obtained by calcining the sol between 700 to 900 °C [6]. Aluminum-substituted magnesium titanate ($Mg_{2-x}Al_{2x}Ti_{1-x}O_4$) was synthesized by conventional dry ceramic method. Analytical grade of carbonates/oxides were taken and wet milled for 20 h using zirconia balls. The resultant slurry was dried and calcined at 1125 °C for 6 h [7]. Spinel structured magnesium titanate was synthesized by using solid state reaction involving MgO and TiO_2. Formation of the particles with high electrical properties was found at 1300 °C alongside with negligible impurities [8].

The conventional synthesis of magnesium titanate typically involves high-purity magnesium and titanium compounds, which can be costly and environmentally demanding to procure. In recent years, there has been a growing emphasis on sustainable manufacturing practices, including the recycling and using industrial byproducts, to mitigate costs and environmental impact [9]. One such byproduct is magnesium chloride, which is generated abundantly

Cite this article as: Neelamegam David, S. G. B., Ponnam, V., Tondepu, S. "Preparation of Magnesium Titanate by Using Magnesium Chloride a Byproduct of Titanium Plant", Periodica Polytechnica Chemical Engineering, 68(4), pp. 582–586, 2024. https://doi.org/10.3311/PPch.37854

as a byproduct in the titanium production plant. Historically, $MgCl_2$ has been disposed of or subjected to energy-intensive treatments for disposal, posing environmental challenges [10]. However, its potential as a precursor for synthesizing magnesium titanate presents an opportunity for cost-effective and sustainable materials synthesis.

This study proposes an innovative approach to utilize $MgCl_2$ derived from titanium plant residues as a magnesium source for $MgTiO_3$ synthesis. By reacting $MgCl_2$ with $TiCl_4$ under controlled thermal conditions, this research aims to develop a practical and environmentally friendly route to produce $MgTiO_3$. The utilization of $MgCl_2$ serves as a sustainable magnesium source while simultaneously mitigating environmental concerns related to waste disposal.

The fundamental purpose of this research is to explore the feasibility of $MgCl_2$ as a precursor for $MgTiO_3$ synthesis, characterize the phase evolution and microstructural properties of the synthesized materials, and explore potential applications in various industrial sectors. Through systematic analysis using techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM), and thermal analysis, this research aims to contribute to sustainable materials synthesis and promote the efficient use of industrial byproducts in ceramic material production.

2 Materials and methods

2.1 Materials

$MgCl_2$ flakes were procured from Kerala Minerals and Metals Limited, Panmana, Kerala. Titanium tetrachloride and oxalic acid were procured commercially.

2.2 Experimental

Initially, 50 g of $MgCl_2$ (equivalent to 12.76 g of magnesium) are dissolved in deionized water, and 60 ml of $TiCl_4$ (equivalent to 25.16 g of titanium) is carefully added to the solution. Under constant stirring, an excess of oxalic acid solution is added to produce magnesium titanyl oxalate. This mixture is filtered and washed with deionized water to remove soluble impurities, then dried at 120 °C to eliminate moisture. The dried precipitate is calcined in a furnace by gradually increasing the temperature to 800 °C and maintaining it for 8 h to decompose the oxalates and form $MgTiO_3$. After cooling to room temperature, the final product is collected and weighed, yielding a mass of 58.54 g.

2.3 Chemical equations involved in the process

The synthesis process consists of the following chemical reactions (Eqs. (1)–(5)):

1. Preparation of magnesium titanyl oxalate:

$$TiCl_4 + H_2O \rightarrow TiOCl_2 + 2HCl, \tag{1}$$

$$\begin{aligned} &MgCl_2 + TiOCl_2 + 2H_2C_2O_4 + 4H_2O \\ &\rightarrow MgTiO\left(C_2O_4\right)_2 \cdot 4H_2O + 4HCl \end{aligned} \tag{2}$$

2. Preparation of magnesium titanate:

$$\begin{aligned} &MgTiO\left(C_2O_4\right)_2 \cdot 4H_2O \\ &\rightarrow MgTiO\left(C_2O_4\right)_2 + 4H_2O, \end{aligned} \tag{3}$$

$$\begin{aligned} &MgTiO\left(C_2O_4\right)_2 \\ &\rightarrow 0.5MgTi_2O_5 + 0.5MgCO_3 + 2CO + 1.5CO_2 \end{aligned} \tag{4}$$

$$0.5MgTi_2O_5 + 0.5MgCO_3 \rightarrow MgTiO_3 + 0.5CO_2 \tag{5}$$

3 Characterization studies

The elemental composition of magnesium titanate was determined using an advanced energy-dispersive X-ray spectroscopy (EDS/EDX) platform equipped with state-of-the-art silicon drift detector (SDD) technology from EDAX Inc., USA. Phase analysis and structural properties were determined using an X-ray diffractometer (Rigaku Miniflex 600, Rigaku Corporation, Japan). To assess the thermal stability of magnesium titanate, a simultaneous thermal analyzer (STA 7200, Hitachi HTG, Japan) was employed. The physical characterization of magnesium titanate took place with a particle size analyzer (Mastersizer 2000 E Ver. 5.60, Malvern Instruments Ltd. UK). Surface morphology examinations were performed using a scanning electron microscope (Vega 3, SBH, TESCAN Brno, S.R.O, Czech Republic).

This comprehensive set of analytical techniques provides a thorough understanding of the elemental, structural, thermal, morphological and physical characteristics of magnesium titanate.

4 Results and discussions

4.1 Chemical characterization

The EDS analysis of the $MgTiO_3$ sample reveals distinct peaks corresponding to the constituent elements as depicted in Fig. 1. The spectrum shows a prominent peak for oxygen at approximately 0.5 keV with an intensity of around 600 counts, indicating a substantial presence of oxygen, which is consistent with the expected stoichiometry of $MgTiO_3$. Additionally, a significant peak for magnesium is observed at about 1.25 keV, with an intensity of around 500 counts, confirming the presence of magnesium in the sample. The spectrum also displays peaks for

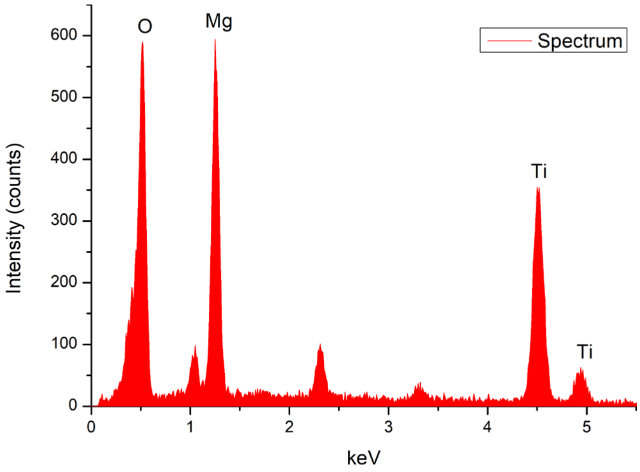

Fig. 1 EDS graph of magnesium titanate

titanium at approximately 4.5 keV and a smaller peak at around 5 keV, corroborating the presence of titanium as part of the magnesium titanate compound. The intensity and position of these peaks align with the standard elemental composition of $MgTiO_3$, confirming the successful synthesis of the compound [11, 12]. The obtained weight and atomic percentages of each element are shown in Table 1.

4.2 Structural characterization

The crystalline nature and structural properties of the synthesized magnesium titanate were evaluated using X-ray diffraction method and the intensity of the diffraction peaks were obtained as shown in Fig. 2. The diffraction shows major peaks at 23.9°, 32.8°, 35.5°, 40.6°, 49.1°, 53.5°, 62°, 63.6° with respective crystalline plane matching values of

Table 1 Quantitative evaluation of magnesium titanate

Element	Weight (%)	Atomic (%)
O	42.14	61.84
Mg	20.6	19.89
Ti	37.26	18.26

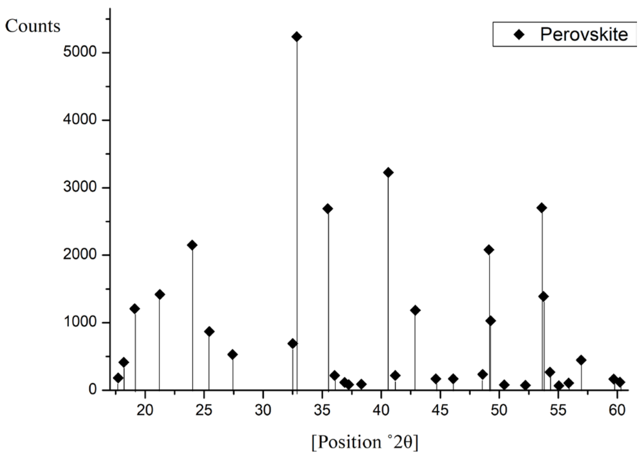

Fig. 2 XRD graph of magnesium titanate

(104), (222), (400), (331), (333), (440), (531) and (622). These intense peaks elevated at 2θ angles ranging from 30° to 40° with the respective *hkl* values, confirm the X-ray diffraction of ABO_3 perovskite crystal structure of the synthesized magnesium titanate with average crystalline size of 64.72 nm [13]. This structure comprises an alkaline earth metal (Mg) and a transition metal (Ti), with octahedral coordination of oxygen atoms around the transition metal, forming a cubic lattice [2, 14, 15]. The resultant phase demonstrates high versatility, offering a broad spectrum of materials with diverse and tunable properties, making it suitable for a wide range of advanced technological applications.

4.3 Thermal characterization

The thermal stability and phase transition of the synthesized magnesium titanate were characterized using TG/DTA analysis at a heating rate of 10 °C/min in nitrogen atmosphere. The resulting curves are shown in Fig. 3. A total mass loss of only 2% was observed from room temperature to 1000 °C. A gradual decrease in the TG curve up to 350 °C, accounting for 1% of the mass loss, is attributed to the loss of moisture and other organic contaminants. Further decomposition observed in the TG curve up to 800 °C, accounting for an additional 1% mass loss, is attributed to the decomposition of oxalate. The crystallization of magnesium titanate into a more stable form was evident in the DTA curve, corresponding to these changes [16].

4.4 Morphological characterization

The external surface and shape of the synthesized magnesium titanate were characterized using a scanning electron microscope (SEM). The image shown in Fig. 4 was formed by the emission of secondary electrons providing detailed topographical information about the external surface. The image reveals that the particles consist of a dense arrangement of polyhedral grains, with sizes ranging from 1 to 5 μm. The grain boundaries are well-defined, and some

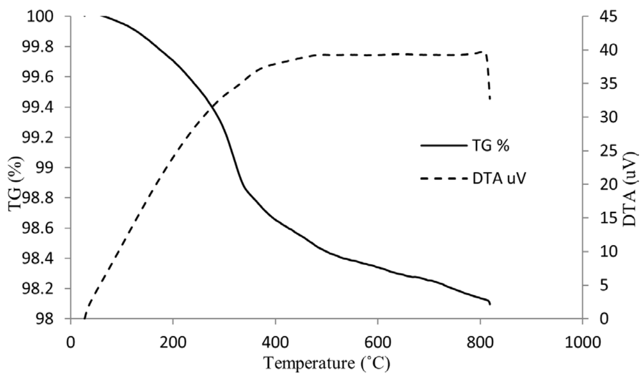

Fig. 3 TG/DTA of magnesium titanate in nitrogen

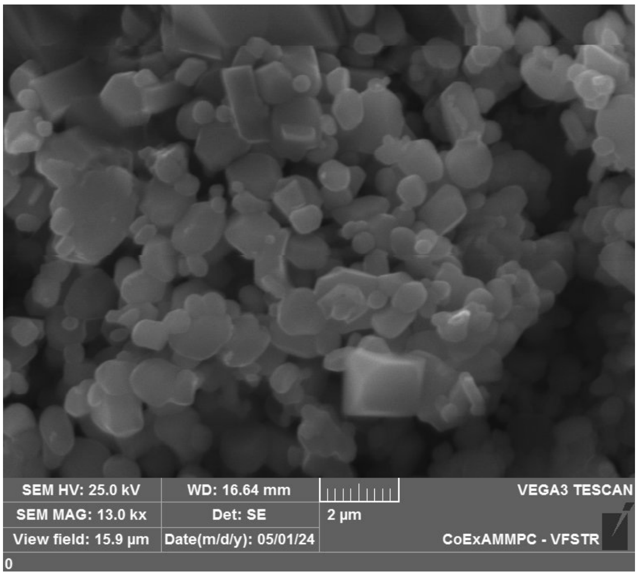

Fig. 4 SEM image of magnesium titanate

grains exhibit faceted surfaces. The surface morphology appears relatively smooth, with no visible cracks or voids, indicating the presence of high-purity crystals [17].

4.5 Physical characterization

Particle size analysis was conducted to examine the distribution and characteristics of the synthesized magnesium titanate. The obtained distribution curve is graphically presented in Fig. 5. The measurements revealed a key parameter, including the median particle size of magnesium titanate, denoted as $d(0.5)$, which was determined to be 4.346 µm. Furthermore, the particle size distribution measurement exhibited noteworthy values of $d(0.1)$ at 1.262 µm, indicating a lower bound, and $d(0.9)$ at 27.951 µm, indicating an upper bound, both of which are considered advantageous. This indicates a higher degree of uniformity in particle size, which subsequently improves the material's performance in a variety of applications [18]. Consequently, samples synthesized at higher temperatures are generally favored due to their ability to yield improved consistency and control in diverse processes and applications.

5 Schematic representation of process flowsheet

The schematic representation of the process flow sheet of the preparation of magnesium titanate from $MgCl_2$, a byproduct of titanium production plant is shown in Fig. 6. The process flow sheet involves the unit operations of precipitation, solid-liquid separation, drying, and calcination. A stoichiometric quantity of $MgCl_2$ solution is mixed with titanium tetrachloride and a sufficient amount of oxalic acid is added to precipitate magnesium titanyl

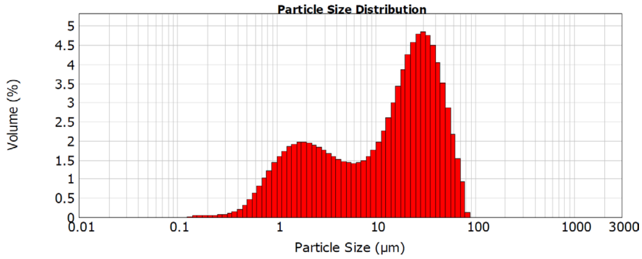

Fig. 5 Particle size distribution of magnesium titanate

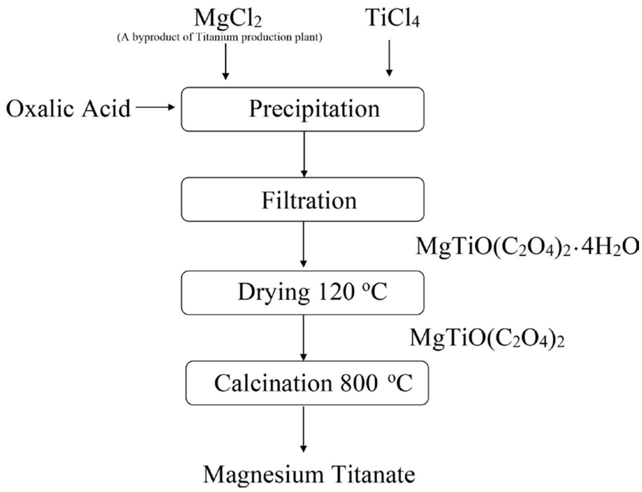

Fig. 6 Process flowsheet to produce magnesium titanate

oxalate. This precipitate is dried at 120 °C for 8 h and later, the dried material is calcined at 800 °C for 6 h to yield single-phase magnesium titanate.

6 Conclusions

The following list contains the conclusions of the article:

- Magnesium titanate was synthesized using an industrial byproduct as a source of magnesium.
- Energy-dispersive X-ray spectroscopy confirmed the presence of the necessary elements with the desired composition.
- The diffraction peaks corresponding to specific crystal planes confirmed the formation of perovskite crystallites, attributed to controlled thermal treatment.
- Microscopy images revealed microcrystals with well-defined polyhedral grains.
- Thermogravimetric analysis (TGA) showed no major weight loss, indicating stability at high-temperature applications.
- The statistical measure of the particle size distribution graph indicated a median particle size of 4.346 µm.
- The synthesized novel material enables global applications in advanced ceramics, electronics, and high-temperature environments.

Acknowledgement and funding information

This work is financially supported by the Defence Research and Development Organisation (DRDO) (Dte of ER&IPR) under Extramural Research Grant No. ERIP/ER/202207003/M/01/1807. The Authors are thankful to the management of VFSTR for the constant encouragement in carrying out the work.

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