

Characterization of Synthesized SrTiO₃ from Purified Celestite Concentrate Using Mechanochemical Process

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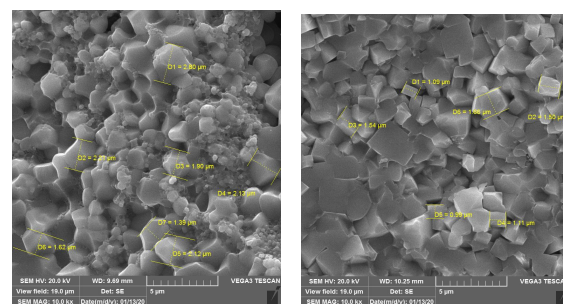
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Abstract: Strontium titanate (SrTiO₃) was synthesized by mechanochemical processing of a mixture of purified celestite concentrate and titanium dioxide. First, SrCO₃ was prepared from a mixture of purified celestite concentrate and sodium carbonate via a mechanochemical method, then SrTiO₃ synthesizes from a stoichiometric mixture of SrCO₃ and TiO₂ powder. After isothermal heating of a 5-h milled mixture of SrCO₃-TiO₂ powder at 900 °C for 2 h, a single phase of SrTiO₃ with a cubic structure was produced. The synthesized SrTiO₃ powders were sintered at different temperatures for 2 h. The produced SrTiO₃ samples were characterized using SEM micrographs, and the phase changes were evaluated using XRD analyses. The changes in the density and dielectric constant of the sintered samples were also determined. The results showed that the properties of SrTiO₃ highly depended on the sintering temperature. Owing to the microstructure and grain size of the produced SrTiO₃ in the milled samples, the dielectric constant of the milled sample was lower than that of the un-milled sample.

Keywords: Ball milling, Celestite concentrate, Perovskite, Strontium carbonate, Strontium titanate

1. INTRODUCTION

Strontium titanate (SrTiO₃) with a perovskite (cubic) structure has been studied regarding its functional dielectric and ferroelectric properties and numerous electronic applications.¹ The majority of these applications are based on their high dielectric constant and low-temperature coefficient of dielectric constant. These applications include random access memory (RAM) devices, oxygen sensors, actuators, and electro-optical devices¹. At room temperature, strontium titanate (SrTiO₃) has a paraelectric cubic structure with a large dielectric constant of ~300 for sintered ceramics.^{2,3} The cubic structure of SrTiO₃ transforms to a tetragonal ferroelectric phase at temperatures below 150K. Also, SrTiO₃ has various physical properties regarding its ferroelectricity, thermoelectricity with thermal conductivity of 12 Wm⁻¹K⁻¹, photocatalysis, and superconductivity at temperatures below 20K². Furthermore, SrTiO₃ has a piezoelectric response, good mechanical strength (Mohs hardness of 5.5), high thermal and chemical stability, low dielectric loss, a low coefficient of thermal expansion, and a high melting temperature of 2080 °C.^{2,4}



(a) Sr₀T₁₄₀₀S
a- un-milled mixture, heating at 900 °C then sintering at 1400 °C.
(b) Sr₅T₁₄₀₀S
b- 5 h milled mixture, heating at 900 °C then sintering at 1400 °C.

The conventional and typical method for processing single-phase strontium titanate (SrTiO₃) is the solid-state reaction using the mixture of TiO₂ and SrCO₃ as starting materials and then prolonged calcination of the mixture at high temperatures (1000-1200 °C).^{2,4,5} The high-temperature calcination is the main drawback of the solid-state method for synthesizing strontium titanate with perovskite structure. Also, as producing SrTiO₃ through a solid-state reaction is typically performed at temperatures above 900 °C, it is impossible to obtain nano-powders using the solid-state reaction method.⁶ The coarse-grained powder synthesized from the solid-state method suffers from agglomerated particles of different sizes and impure phases due to incomplete reactions.⁴ In addition to the solid-state route, there are many methods to synthesize strontium titanate, e.g., polymer solution⁵, molten salt,⁷ hydrothermal,⁸ microwave,⁹ coprecipitation,¹⁰ sol-gel,¹¹ mechanochemical,^{12,13} sonochemical synthesis at low-temperature¹⁴ and other methods such as alkoxide hydrolysis, metallo-organic processing, and combustion methods.^{1,2,4,7} It is anticipated that the microstructure of the final product and the processing for each method is quite different. The convenient method to produce fine

and nanocrystalline materials is mechanical milling by a ball-milling technique. This route has also been adapted to produce strontium titanate.²

There are some studies on synthesizing advanced materials using mechanochemical methods and ball milling operations.¹⁵⁻²⁰ For instance, Psiuk et al. synthesized strontium titanate (SrTiO₃) using a solid-state reaction from an equimolar portion of SrCO₃ and TiO₂ and studied the effect of milling on the particle size.²¹ In another effort, the effect of mechanical activation on the microstructural properties of SrTiO₃ powders was investigated. The results showed that the prolonged mechanical activation decreased the average crystallite size from 75 nm to 20 nm and increased mesopore volume and specific surface area²². In another study, Berbenni et al.²³ demonstrated that by annealing the high-energy milled mixtures of SrCO₃-rutile (TiO₂) at 800-850 °C for about 12 h, SrTiO₃ and Sr₂TiO₄ phases are formed. However, none of these products could be obtained by heating the physical mixtures to temperatures as high as 1000 °C. The effect of milling time on microstructure, crystallite size, and dielectric properties of SrTiO₃ was also studied by Wong et al.²⁴ These authors indicated the reduction in grain size by prolonging the milling time and this reduction in grain size improved the dielectric constant.²⁴

The previous results indicated that synthesizing SrTiO₃ using mechanochemical and ball milling techniques is possible, and producing very fine SrTiO₃ powders from celestite concentrate at a lower temperature than the solid-state method seems feasible. Although the synthesis of SrTiO₃ powder using mechanochemical process has been reported in previous work¹³, the final characterization of the sintered products and comparison with other works need a comprehensive investigation. In this article, SrCO₃ was synthesized from purified celestite concentrate, followed by forming SrTiO₃ by heating the mixture of SrCO₃ and TiO₂. The synthesized SrTiO₃ powders were sintered at different temperatures, then the phase changes and the microstructure characterizations of the sintered samples were studied in detail. Furthermore, the changes of the density and the dielectric behavior of the sintered samples at different temperatures were investigated. The effects of sintering temperatures on the density and the dielectric constant of the final products were also studied in this article.

Table 1. XRF analysis of the purified celestite concentrate. (N = not trace)

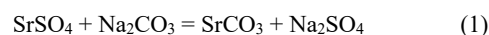
Composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	MnO	P ₂ O ₅	LOI	SrO	SO ₃
Percent	N	0.241	N	0.1176	N	0.003	N	0.017	0.007	0.006	1.91	54.98	42.51

Table 2. The mass percents of raw materials for different mixtures based on the reactions (1) and (2)

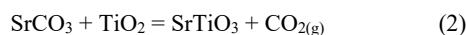
Reaction	Mixture (molar ratio)	%SrSO ₄	%Na ₂ CO ₃	%SrCO ₃	%TiO ₂
SrSO ₄ + Na ₂ CO ₃ = SrCO ₃ + Na ₂ SO ₄	SrSO ₄ +Na ₂ CO ₃ = 1:1	63.4	36.6	-	-
	SrSO ₄ +Na ₂ CO ₃ = 1:2	46.4	53.6	-	-
SrCO ₃ + TiO ₂ = SrTiO ₃ + CO _{2(g)}	SrCO ₃ +TiO ₂ = 1:1	-	-	64.9	35.1

2. EXPERIMENTAL

The celestite concentrate (~95% SrSO₄) was prepared from the Likak mne (Kohgiluyeh and Boyer-Ahmad Province). After crushing and milling the celestite concentrate, the acid washing (at 25 °C) was done with ~1 N hydrochloric acid. Table 1 shows the XRF analysis of the purified celestite concentrate after acid washing. As shown in Table 1, the purified celestite concentrate contains ~98% SrSO₄, and after acid washing, the amounts of other impurities, such as barium (Ba), are about 100 ppm. The loss on ignition (LOI) in XRF analysis was determined as the mass reduction percentage of a sample after heating at 1100 °C for 2 h. After acid washing, the purified celestite concentrate was mixed with Na₂CO₃ based on reaction (1). The mixture of raw materials (4.8 gr) based on reaction (1) was prepared and milled in a planetary ball mill at different times (10, 20, 30, 60 and 90 minutes). The mass percents of raw materials based on reaction (1) are listed in Table 2. For a mixture with weight of 4.8 gr, the mass of purified celestite concentrate and Na₂CO₃ were determined based on Table 2.



After finishing milling run, the as-milled powders were gathered from the milling cup carefully. The weight of the mixture after each milling run was about 4 grams and some of the fine particles were sticking to cup and balls. One gram of the as-milled sample was dissolved in 20 mL water at room temperature (25 °C) to remove the water-soluble compounds (i.e., Na₂SO₄ and/or un-reacted Na₂CO₃ phases). The water dissolution process lasted 1 h for each sample; then, the precipitated strontium carbonate was removed from the solution. After preparing strontium carbonate (SrCO₃) using reaction (1), the stoichiometric mixtures of SrCO₃ and TiO₂ (anatase) were prepared based on reaction (2). For preparing this stoichiometric mixture with weight of 4.8 gr, the mass of SrCO₃ and TiO₂ samples were determined based on the data in Table (2). The milling of the mixtures was done in a planetary ball mill at different times. After finishing the milling run, about 4 grams of the as-milled sample was gathered from the milling cup. Titanium dioxide (TiO₂) powder was mainly of anatase type, although some minor signs of rutile phase were observed in its XRD pattern.²⁵ Figure 1 shows the sequence of the strontium titanate (SrTiO₃) production in this research.



Mechanical milling of the mixtures and mechanochemical reactions were performed in a closed chamber using a planetary ball mill (Farapazhouhesh, FP2 model) at different milling times. The ball milling conditions were chosen based on our previous works,¹³ and their details listed in elsewhere.²⁵

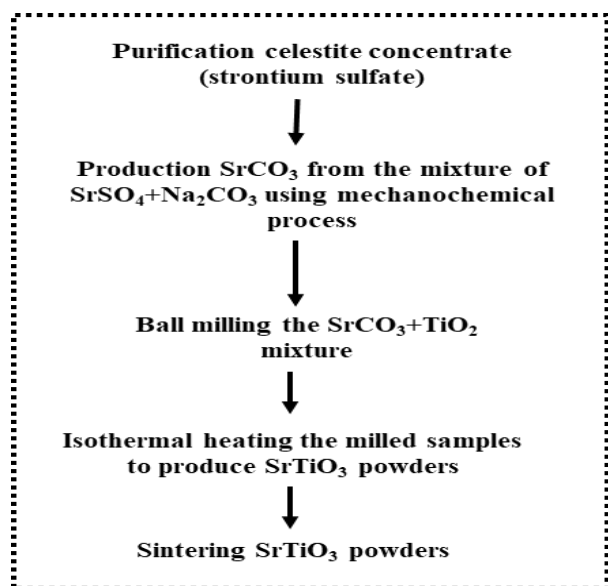


Figure 1. This scheme explains the sequence for synthesizing strontium titanate (SrTiO_3) [13,25].

The undesirable acid-soluble phases were removed by performing the acid-washing process of as-milled powders with diluted hydrochloric acid ($\sim 1\text{ N HCl}$) at room temperature ($25\text{ }^\circ\text{C}$).

Preliminary works showed that SrCO_3 , SrSO_4 , and SrTiO_3 were not soluble in diluted hydrochloric acid ($\sim 1\text{ N HCl}$).²⁵ The acid-washed residues were oven dried at $110\text{ }^\circ\text{C}$ for 2 h, followed by collecting the dried powder in a sealed box. The isothermal heating of the SrCO_3 - TiO_2 mixtures was done at $900\text{ }^\circ\text{C}$ for 2 h in a tube furnace (Lenton, LFT, 16-180) under an air atmosphere. Next, the samples were cooled in the tube furnace to room temperature and the synthesized SrTiO_3 powder was prepared for sintering to produce the bulk sample. Several works reported the optimum preparation, compaction, and sintering conditions of the SrTiO_3 powders to produce bulk SrTiO_3 samples. The details and results of all trials have been listed elsewhere.²⁵ The results showed that the optimum temperatures for sintering these compacted samples are in the range of 1300 - $1400\text{ }^\circ\text{C}$.²⁵ The bulk density of sintered samples was measured using the Archimedes method. In addition, the dielectric behavior of strontium titanate samples was carried out at the frequency of 1 kHz using LCR-meter (HP-4294) and the dielectric constants of the sintered samples were calculated. Moreover, phase changes of the samples were studied using X-ray diffraction (XRD, Phillips Analytical, 40 kV , 40 mA , X'Pert APD) using $\text{Co-K}\alpha$ radiation over a 2θ range of 20 - 100° . Finally, XRF analysis of purified celestite concentrate was done using PHILIPS PW1410, the microstructures of the samples were studied using scanning electron microscope (TESCAN-VEGA3) and the grain size distribution was calculated using ImageJ software.

3. RESULTS AND DISCUSSION

Thermodynamics assessments

Thermodynamics assessments using HSC software²⁶ indicate that reaction (1) is exothermic and favorable at room temperature ($\Delta G_{298\text{ K}}^\circ = -22.2\text{ kJ}$). These assessments,

on the other hand, show that reaction (2) is endothermic at room temperature ($\Delta H_{298\text{ K}}^\circ = 104.85\text{ kJ}$) and this reaction is feasible at temperatures above $330\text{ }^\circ\text{C}$ ($\Delta G_{608\text{ K}}^\circ = -0.89\text{ kJ}$).²⁶ Therefore, it is anticipated that the mechanochemical process during milling operation leads to the formation of SrCO_3 using reaction (1).

Production SrCO_3 from mixture of $\text{SrSO}_4 + \text{Na}_2\text{CO}_3$

Previous works showed that reaction (1) occurs after 1 h milling; however, it can be completed once the amount of Na_2CO_3 is more than the stoichiometric ratio.^{13,27} Figure 2 shows the XRD patterns of the dried solid products in reaction (1) for different stoichiometric ratios of Na_2CO_3 after the dissolution of the 1-h milled samples in water. The phase changes after 1 h of milling were studied using the XRD pattern of purified celestite concentrate (Figure 2).

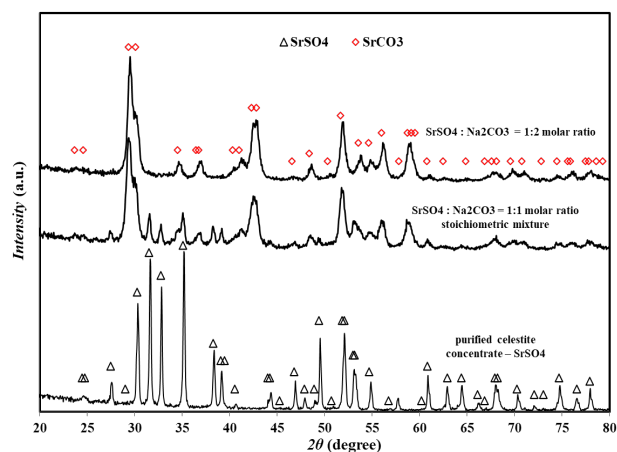


Figure 2. XRD patterns of the dried solid products for different molar ratios of Na_2CO_3 (based on reaction 1) after dissolution of the 1 h milled samples in water. XRD pattern of purified celestite is also indicated.

Although the most of the celestite peaks (SrSO_4) disappeared (Figure 2) in the stoichiometric ratio ($\text{SrSO}_4 + \text{Na}_2\text{CO}_3$), increasing the amount of Na_2CO_3 results in the completion of the reaction (1). After dissolving the 1 h milled mixtures in water, the SrCO_3 phase peaks are clearly observed in the solid products of the mixture with a mole ratio of $\text{SrSO}_4:\text{Na}_2\text{CO}_3 = 1:2$. It is noteworthy that SrSO_4 and SrCO_3 phases are not soluble in water at room temperature ($25\text{ }^\circ\text{C}$) due to their solubility product constants.^{28,29}

After drying the solid residues of water washing, XRD analysis was undertaken to study the synthesized SrCO_3 sample. The comparison between the synthesized SrCO_3 sample via reaction (1) and the MERCK grade (107861) of SrCO_3 is illustrated in Figure 3. Although the shape of particles of SrCO_3 produced from reaction (1) was clustered and agglomerated, the main peaks of the SrCO_3 phase (JCPDS No. 05-0418) are clearly observed in the synthesized SrCO_3 sample in Figure 3.

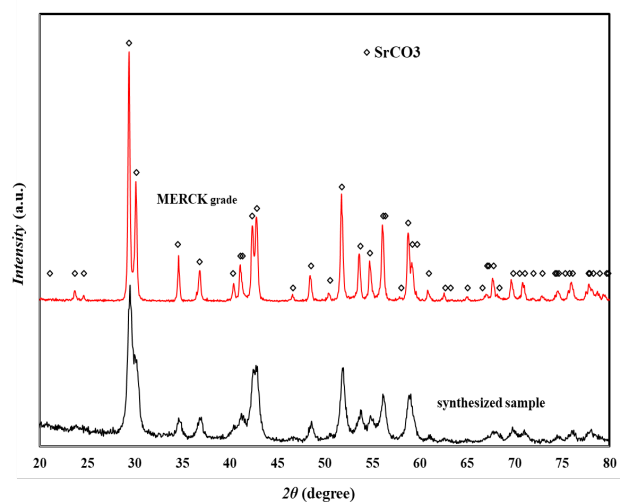


Figure 3. Comparison between XRD patterns of the synthesized SrCO_3 via reaction (1) and the MERCK grade.

Synthesis SrTiO_3

After synthesizing SrCO_3 using mechanochemical process by reaction (1), the mixture of $\text{SrCO}_3\text{-TiO}_2$ with stoichiometric ratio was prepared based on reaction (2). The stoichiometric ratio of $\text{SrCO}_3\text{-TiO}_2$ was milled in a planetary ball mill for 5 and 10 h, followed by collecting the as-milled samples from milling cups. The previous results indicated that the traces of SrCO_3 and TiO_2 phases observed in the XRD patterns of the as-milled mixtures of $\text{SrCO}_3\text{-TiO}_2$ and the formation of SrTiO_3 and/or its intermediate phases are not feasible after 10 h of milling. The evidence of peak broadening and decreasing in the intensity of peaks was observed by prolonging the milling time to 10 h.¹³ These findings are consistent with those of Wong et al.,²⁴ in which single-phase SrTiO_3 formed after 16 h of milling through an annealing process. The signs of the rutile phase are observed in the milled samples,¹³ suggesting that anatase-rutile phase transformation occurs during milling. The traces of anatase to rutile phase transition in the milled sample of TiO_2 are consistent with the previous results.³⁰⁻³² Also, the transformation of anatase to rutile was attributed to increasing the milling time to 16 h in the other results.²⁴ Additionally, our results showed that prolonging the milling time leads to increasing iron contaminations in the 10 h milled mixtures but do not affect the formation of the SrTiO_3 phase.²⁵

If reaction (2) occurs completely, the stoichiometric mass loss of SrTiO_3 formation is estimated to be about 20%. The TGA/DTA analysis results showed this mass loss is obtained at $\sim 860^\circ\text{C}$ in a 5-h milled sample; however, in the un-milled sample, reaction (2) can be completed after heating at 1000°C .^{13,25} According to the DTA analysis of previous studies on the formation of SrTiO_3 ceramic powder using the gel solid-state reaction method, the reaction is completed at about 940°C .³³ Thermodynamics assessments using HSC software²⁶ indicated that reaction

(2) could occur at temperatures above 330°C . Since the raw materials in reaction (2) are in the solid state, contact between adjacent particles is inevitable. Milling raw materials decreases particle size and increases particles' surface area. These effects in milled samples play a significant role in the kinetics of solid-solid reactions. Therefore, it is anticipated that the formation of SrTiO_3 in the 5-h milled sample occurs at a lower temperature than in the un-milled sample.

The 5-h milled sample and an un-milled mixture of $\text{SrCO}_3\text{-TiO}_2$ were heated at 900°C for 2 h under an air atmosphere in a tube furnace. The signs of the SrTiO_3 phase (JCPDS No. 86-177) with the cubic structure are clearly observed in XRD patterns after heating at 900°C (Figure 4). Previous results have also indicated that a single phase of SrTiO_3 cannot be formed with milling alone and requires an annealing process.²⁴

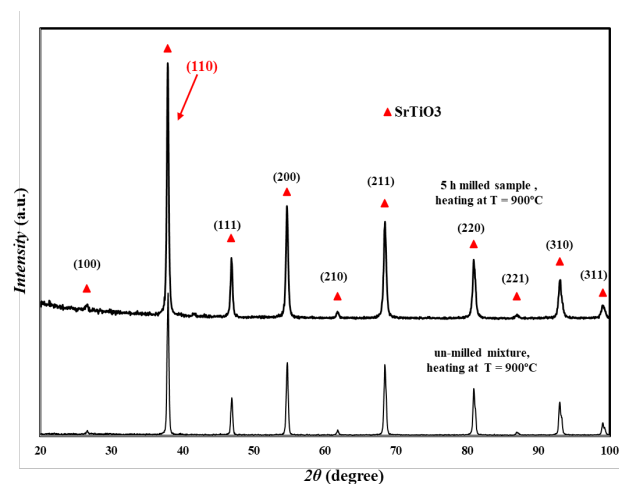


Figure 4. XRD patterns of 5-h milled sample and un-milled mixture of $\text{SrCO}_3\text{-TiO}_2$ after isothermal heating at 900°C for two hours.

Characterizing the synthesized SrTiO_3 powder

Perovskite strontium carbonate (SrTiO_3) has a cubic structure and its lattice parameter based on the standard card file number 86-177 is 3.8996 \AA . The lattice parameter of produced SrTiO_3 after heating at 900°C was determined using the Bragg equation based on XRD data files of Figure 4. The lattice parameter of synthesized SrTiO_3 from the 5 h milled mixture was about 3.8843 \AA . However, the corresponding value for synthesized SrTiO_3 from an un-milled mixture with a similar heating regime was 3.8912 \AA . These computed lattice parameters for both synthesized SrTiO_3 samples using the results of Figure 4 are very close to the value of card file No. 86-177. In this respect, Zivojinovic et al.²² showed that mechanical activation of SrTiO_3 at different times increases the lattice parameter from $\sim 3.9057 \text{ \AA}$ in an un-milled sample to $\sim 3.9067 \text{ \AA}$ for 120 min of mechanical activation. However, Wong et al.²⁴ showed the lattice parameter of SrTiO_3 samples after sintering at 1200°C was 3.905 \AA

and the milling time of raw materials had no effect on the lattice parameter of sintered samples.

The SEM micrographs of synthesized SrTiO₃ after heating at 900 °C are shown in Figure 5. As can be seen, the particle size of the 5-h milled SrTiO₃ sample (Figure 5b) is smaller than the un-milled mixture.

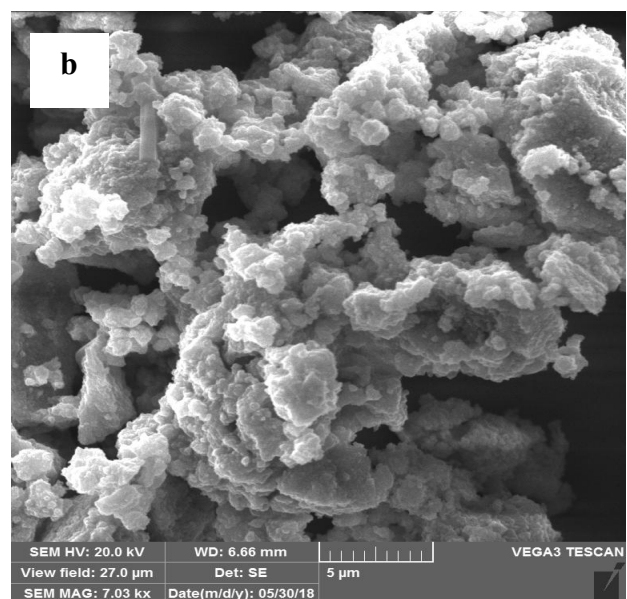
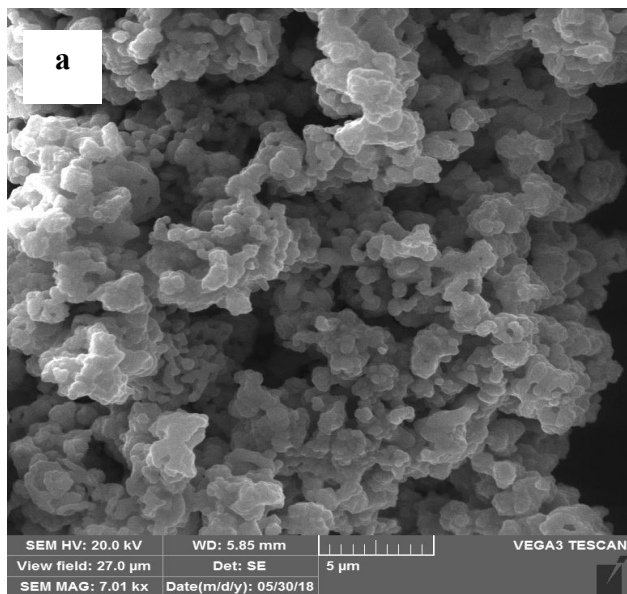


Figure 5. SEM micrographs of the synthesized SrTiO₃ after heating at 900 °C for two hours. (a) un-milled mixture, (b) 5-h milled sample.

The morphologies of particles in SEM micrographs of Figure 5 and the decreased particle size of SrTiO₃ in the 5-h milled sample are very similar to those reported by Zivojinovic et al.²². Their results showed that the particle size of SrTiO₃ decreases after mechanical activation, depending on activation time. Therefore, the XRD

patterns of Figure 4 confirm the presence of single-phase SrTiO₃ after heating at 900 °C. In addition, the micrographs in Figure 5 suggest that milling the mixtures of SrCO₃-TiO₂ before heating plays a significant role in decreasing the particle size of synthesized SrTiO₃.

Characterizing the sintered samples of SrTiO₃

After synthesizing SrTiO₃ powders at 900 °C, these powders were washed with diluted hydrochloric acid (HCl, ~1 N) at room temperature (25 °C) to remove the iron contamination of the ball milling process. The solid residues were oven dried at 110 °C for 2 h. Then, the final fine-grained powders were compacted to produce a disc shape sample ($\varnothing \approx 10\text{mm}$). The sintering operation was done at different temperatures for 2 h. Table 3 shows the specifications of the synthesized SrTiO₃ samples after sintering at different temperatures.

Table 3. The specifications of the synthesized SrTiO₃ samples after sintering at different temperatures

Specification of sample	Sr ₀ T ₁₃₀₀ S	Sr ₅ T ₁₃₀₀ S	Sr ₀ T ₁₄₀₀ S	Sr ₅ T ₁₄₀₀ S
Preparation of SrTiO ₃ powders from mixture of SrCO ₃ -TiO ₂ before sintering	un-milled mixture after heating at 900 °C	5 h milled mixture after heating at 900 °C	un-milled mixture after heating at 900 °C	5 h milled mixture after heating at 900 °C
Sintering time/temperature	2 h at 1300 °C		2 h at 1400 °C	
Density (g/cm^3)	3.441	3.53	4.67	4.61
Relative Dielectric constant	407.2	130.5	355.5	310.86

After sintering the samples at 1300 °C, the density of these samples was determined using the Archimedes method. The densities and dielectric constants of sintered samples are also presented in Table 3. The density of the SrTiO₃ sample produced from 5 h milled mixture of SrCO₃-TiO₂ after sintering at 1300 °C was about 3.53 g/cm³. Besides, the corresponding value for the produced sample from the un-milled mixture of SrCO₃-TiO₂ at the same sintering temperature (Sr₀T₁₃₀₀S) was about 3.441 g/cm³ (Table 3).

Figure 6 shows the SEM micrographs from the cross-sectional area of Sr₀T₁₃₀₀S and Sr₅T₁₃₀₀S samples. The presence of voids and cracks in the micrographs of Figure 6 indicates that sintering was not completed at 1300 °C, and the samples are not dense enough. Therefore, increasing the sintering temperature can improve the bulk density of samples. As it is shown in Table 3, after sintering at 1400 °C, the densities of bulk samples increased considerably and reached about 4.6 g/cm³. Nevertheless, raising the sintering temperature to 1500 °C deteriorated the samples, and the density dropped considerably in our research. Therefore, 1400 °C is regarded as the optimum sintering temperature in this study.

The previous results showed that the bulk density of the SrTiO₃ sample sintered at 1400 °C with no observable

porosities is about 4.8 g/cm^3 .⁵ In another study, the density of synthesized SrTiO_3 samples was about 5.11 g/cm^3 after sintering the pellets at $1200 \text{ }^\circ\text{C}$ with a heating rate of $5 \text{ }^\circ\text{C/min}$ for 20 h using carbolite furnace²⁴. George et al.⁴ synthesized SrTiO_3 via a modified combustion method and performed sintering at $1350 \text{ }^\circ\text{C}$ for 3 h. The density of this SrTiO_3 sample was 98% of the theoretical density. As a result, many parameters such as compaction operations, temperature/time of sintering, heating/cooling rate during the sintering process, and the type of sintering furnace have a significant role in the sintering operation of SrTiO_3 powders.

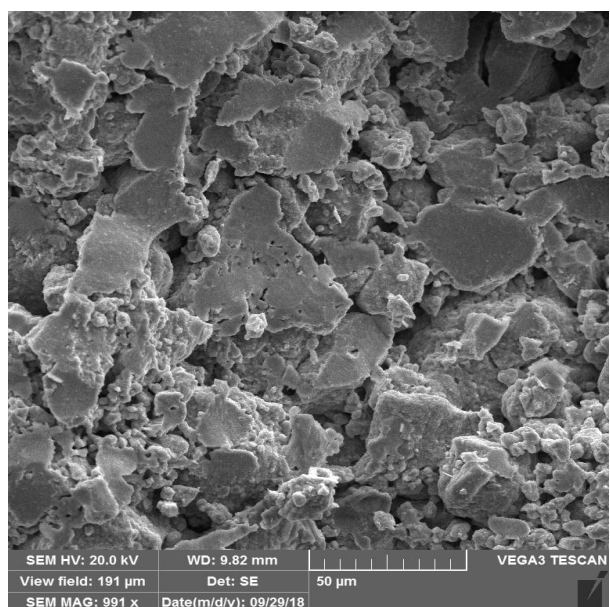
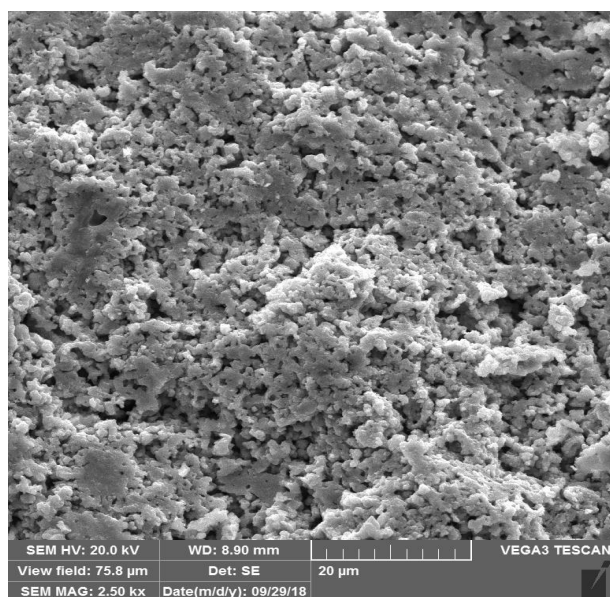


Figure 6. SEM morphology from cross sectional area of SrTiO_3 samples after sintering at $1300 \text{ }^\circ\text{C}$. (a) ($\text{Sr}_0\text{T}_{1300\text{S}}$), (b) $\text{Sr}_5\text{T}_{1300\text{S}}$. The specifications of samples are listed in Table 3.

Figure 7 shows the SEM micrographs of SrTiO_3 samples after sintering at $1400 \text{ }^\circ\text{C}$ for 2 h. These micrographs are from the cross-section of $\text{Sr}_0\text{T}_{1400\text{S}}$ and $\text{Sr}_5\text{T}_{1400\text{S}}$ samples, for which the details of sintering process are mentioned in Table 3. The size distributions of the SEM micrographs for each sample are also demonstrated in Figure 7. The grain morphology and shapes of grains in Figure 7 are similar to those reported in previous studies.^{4,5,24} As shown in Figure 7, the initial milling process affected the morphology of the grains. The polyhedral grains of the un-milled sample ($\text{Sr}_0\text{T}_{1400\text{S}}$) are changed to the pseudo-cubic grains in the 5-h milled sample ($\text{Sr}_5\text{T}_{1400\text{S}}$) with an average grain size of $1.5 \mu\text{m}$. The grain size analysis of the SEM micrographs in Figure 7 shows that the grain size distribution in the $\text{Sr}_5\text{T}_{1400\text{S}}$ sample is more uniform than the un-milled sample ($\text{Sr}_0\text{T}_{1400\text{S}}$). Although the average grain size of the both samples is in the range of $1\text{--}1.5 \mu\text{m}$, the grain size analysis and the SEM micrographs in Figure 7 imply the milling process of the raw mixtures ($\text{SrCO}_3+\text{TiO}_2$) before the synthesis of SrTiO_3 has a major effect on the morphology and the grain size distribution of the sintered products at $1400 \text{ }^\circ\text{C}$.

The mixtures of $\text{SrCO}_3\text{--TiO}_2$ were isothermally heated at $1500 \text{ }^\circ\text{C}$ for 2 h under an air atmosphere in a tube furnace. The XRD results of Figure 8 indicate that after the formation of SrTiO_3 from isothermal heating at $900 \text{ }^\circ\text{C}$, no phase change occurs during isothermal heating at elevated temperatures such as $1500 \text{ }^\circ\text{C}$. Therefore, the XRD results in Figure 8 confirm that the particles in the micrographs of Figure 7 are SrTiO_3 phase.

Previous studies have evidenced that grain size reduction due to increasing milling time decreases the dielectric constant. As the dielectric constant of SrTiO_3 samples at 1 MHz decreased from 78.8 to 63, the milling time increased from 8 to 16 h, respectively²⁴. Tkach et al.³⁴ studied the effect of non-stoichiometry on the microstructure and dielectric properties of SrTiO_3 at low temperatures and reported loss factor values of the order of 10^{-3} at temperatures below 100 K at a frequency of 10 kHz. Furthermore, George et al.⁴ showed that the fine-grained SrTiO_3 has a dielectric constant of 281 at 5 MHz. The sintered SrTiO_3 sample of their work reached 98% of the theoretical density at a relatively lower temperature of $1350 \text{ }^\circ\text{C}$ for 3 h⁴.

The results of Table 3 show that dielectric constants of the 5-h milled samples are lower than in the un-milled samples. The results of Table 3 also suggest that the dielectric constant is very sensitive to sintering temperature. According to Table 3, increasing the sintering temperature from $1300 \text{ }^\circ\text{C}$ to $1400 \text{ }^\circ\text{C}$, results in higher bulk density of the SrTiO_3 samples. The effect of sintering temperature on the microstructure of the final product is also justified by studying the SEM micrographs of the sintered samples in Figures 6 and 7. The results of

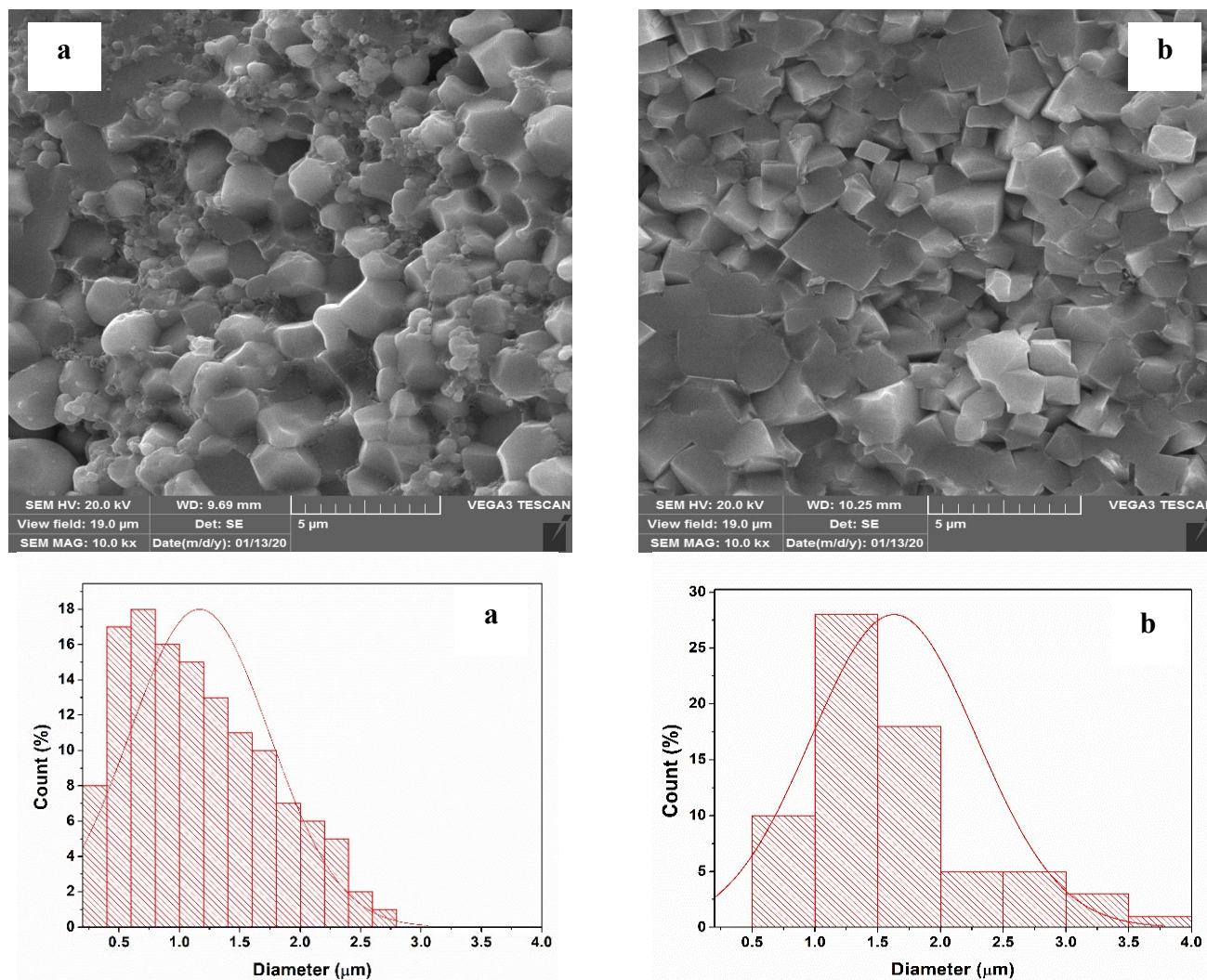


Figure 7. SEM micrographs of the cross-sectional area of the samples (a) $\text{Sr}_0\text{T}_{1400}\text{S}$ and (b) $\text{Sr}_5\text{T}_{1400}\text{S}$ with their grain size distributions after sintering at 1400°C for two hours. The specification of the samples is listed in Table 3.

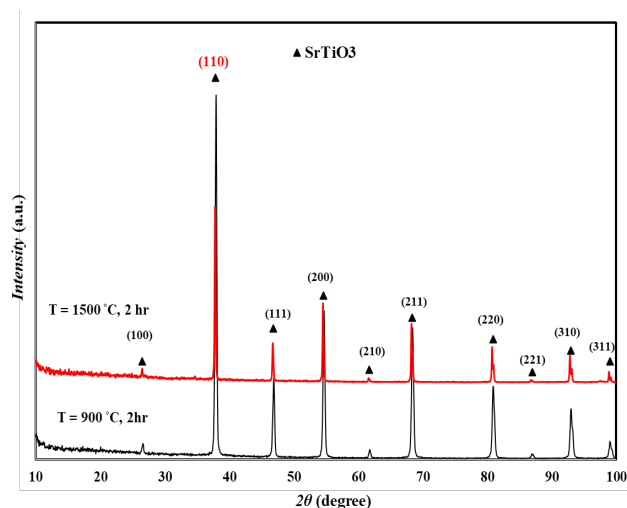


Figure 8. The comparison of XRD patterns for SrTiO_3 after isothermal heating at different temperatures.

Table 3 and Figures 6-7 indicate that both milling operation and sintering temperature play an essential role in the physical and electrical properties of SrTiO_3 . Therefore, the results of this work and data in Table 3 are in the range of other research and consistent with previous works.

4. CONCLUSION

Strontium titanate (SrTiO_3) with cubic structure was synthesized from a mixture of purified celestite concentrate. First, SrCO_3 was produced from purified celestite concentrate using mechanochemical process. Next, SrTiO_3 was synthesized from a stoichiometric mixture of $\text{SrCO}_3\text{-TiO}_2$ via isothermal heating of the milled sample and un-milled mixtures at 900°C . The lattice parameters of the synthesized SrTiO_3 were very close to the corresponding amounts of SrTiO_3 with the standard card file number JCPDS No. 86-177. Milling of

the raw mixture (SrCO₃-TiO₂) decreased the particle size of SrTiO₃ powders, and the results indicated that the ball milling operation has a significant role in the characteristics of the sintered products. The density of synthesized SrTiO₃ reached about 4.6 g/cm³ after sintering at 1400 °C for 2 h, which deteriorated at higher temperatures. Based on the obtained results, the dielectric constants strongly depended on milling operation and sintering temperature. The dielectric constant of sintered SrTiO₃ sample, fabricated from the 5-h milled mixture of SrCO₃-TiO₂, was lower than the sample from the unmilled mixture. This result can be attributed to microstructure and density of this sample. The dielectric constant of the 5 h milled mixture after sintering at 1400°C was about 310.

CONFLICTS OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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