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STRUCTURAL AND MORPHOLOGICAL PROPERTIES OF ZINC STANNATE NANOFIBERS

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Abstract

Zinc stannate nanofibers have unique properties due to their size, distribution, and morphology and are a very important component in the rapidly developing fields of nanotechnology. In this research, zinc stannate nanopowders using zinc chloride and tin chloride were used as the starting materials of the zinc and tin sources. Zinc stannate nanofibers are grown onto fluorine-doped tin oxide (FTO) glass substrates from an aqueous solution of zinc stannate and polyvinyl alcohol (PVA) is used to produce zinc stannate nanofibers. Firstly, zinc stannate nanopowders were prepared by using the sol-gel technique. Then, zinc stannate nanofibers were fabricated by using the electrospinning method. The structural properties of zinc stannate nanopowders were characterized by instrumental analysis such as X-ray Diffraction (XRD). The morphological properties of zinc stannate nanofibers were examined by Scanning Electron Microscopy (SEM). Generated zinc stannate nanomaterials were investigated to different degrees due to their environmental friendliness, and low cost, especially in the context of enhancing their efficiency and durability, zinc stannate nanofibers are a promising class of photovoltaic cells with the capability of generating energy and have attracted numerous kinds of research.

Keywords: Zinc Stannate Nanofibers, Sol-gel Method, Electrospinning Method, XRD, and SEM

Introduction

Nanofibers offer small pore sizes and large surface areas with novel and significantly improved physical, chemical, and biological properties as the fiber diameter decreases to the nano level [Ondarcuhu, T. et al, 1998]. Fiber with a diameter in the nanometer range. Many types of polymers were processed into nanofibers of 50 to 1000 nanometers in diameter, several orders of magnitude smaller than conventional fiber spinning. Polymer nanofibers possess many unique properties since these fibers have a very large surface area per unit mass, as well as a small pore size [Q. WEI, et al, 2012]. Polymer nanofibers with specific surface properties are of importance in many technical applications as the surface features affect wettability, adsorption, electrical conductivity, optical properties, and biocompatibility. Modification of polymer nanofibers improves the surface properties of these materials to meet some special applications [F. Huang, et al, 2012]. Nanofibers can be produced from almost all polymers. However, their properties and applications are different. The diameters of nanofibers depend on the type of polymers used and their production method. They can be produced using various techniques [W.S. Khan, 2010].

There are various processes available to generate nanofibers. These processes include template synthesis, phase separation, and self-assembly. However, electrospinning is the simplest, most straightforward, and cheapest process of producing nano- and micro-sized fibers in a very short period with minimum investment [W.S. Khan, et al, 2010]. Generally, electrospinning is used to produce high-surface-area submicron and nanosized fibers. These fibers possess more exceptional physical properties (e.g., mechanical, magnetic, electrical, optical, and thermal) than their bulk-size fibers. Electrospinning is related to the principle of spinning polymeric solutions or melting at elevated temperatures in a high DC electric field

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[W.S. Khan, et al, 2012.]. Electrospinning is a process in which a high voltage, and consequently a high electrostatic field, is applied to a polymeric solution or melt to generate nanofibers in a very quick time. The term “electrospinning” was derived from “electrostatic spinning” because of the electrostatic field utilized during the fabrication process [J.H. He, et al, 2008]. Electrospinning is a relatively simpler, easier, and more direct process of fabricating a nonwoven mat of polymer fibers compared to conventional methods, such as melt spinning, wet spinning, and extrusion molding with the minimum initial investment and in the shortest possible time. Electrospinning generally produces fibers with diameters in the range of 40-2000 nm. Several different shapes and sizes of micron and nanoscale fibers can be fabricated from various classes of polymers [D.H. Reneker, et al, 1996].

Polymer nanofibers can be fabricated using several different methods such as self-assembly, template synthesis, drawing, phase separation, melt blowing, solvent casting, and electrospinning. Among these, electrospinning appears to be one of the most convenient and cost-effective methods because it can fabricate long and continuous nanofibers with adjustable diameters and is widely used to produce polymer nanofibers [S. S. Dissanayake, et al, 2015]. Electrospinning is the technique that uses a strong electric field to produce polymer nanofibers from a polymer solution or polymer melt. If electrostatic forces overcome the surface tension of a polymer solution a charged jet is ejected and moves toward a grounded electrode. The electrospun nanofibers can be collected on a substrate located on the counter electrode [Baumgarten, P. K, et al, 1971]. An electrospinning apparatus consists of the following four major components: High-voltage power supply, Flow control pump, and Spinneret, Collector. The apparatus as well as the components can be set up and adjusted by the actual needs. With high-voltage potential applied, the polymer solution or melt inside the spinneret is forced through a flow control pump to form a pendant drop at the tip of the spinneret. Free charges are induced into the polymer solution as a result of the applied high-voltage potential. In response to the applied electric field, these charged ions move toward the electrode of opposite polarity, transferring stretching forces generated by the electrical field to the polymer liquid. As the applied electric field increases, the hemispherical surface of the fluid at the tip of the spinneret is stretched and a conic shape called a Taylor cone is formed. When the applied high-voltage potential reaches a critical value, the electrostatic forces overcome the surface tension, and a charged jet of the solution ejected from the tip of the Taylor cone is rapidly accelerated to the grounded collecting target. Due to instabilities in the jet, the charged jet undergoes violent whipping and elongation, allowing the evaporation of solvent or cooling of melts to form solid fibers on the collector [Huang, Z. M, et al, 2003].

Materials and Methods

Sample Preparation of zinc stannate nanopowders

Materials

In this research work, analytical standard grades of zinc chloride, tin chloride, potassium hydroxide (KOH), and hydrochloric acid (HCl) were used as the starting materials to synthesize zinc stannate nanopowders. Distilled water was used as the dissolving solvent. All chemicals and solvents were purchased from the Academy chemical shop in Yangon. All reagents were commercial grade and were used without further purification.

Methods

The synthesis method consisted of two steps (1) The preparation of zinc stannate nanopowders was synthesized by the sol-gel technique and (2) zinc stannate nanofibers were fabricated by using the electrospinning method.

Sample Preparation of zinc stannate nanopowders

In this recent research work, Zinc Stannate samples were prepared by a wet chemical sol-gel method. Zinc Chloride and Tin Chloride were used as the zinc and tin sources respectively. 0.2 M of both materials were mixed with 200 ml of distilled water in beakers respectively. After that, the beaker was put over the magnetic stirrer and stirred at 400 rpm for 30 minutes. Both precursors were first dissolved in distilled water to form two transparent solutions and then mixed. The solutions were prepared by thoroughly mixing both solutions in a beaker. The solution was precipitated at room temperature by adding dropwise 0.5M KOH until a pH value in the system of 14 was reached and stirred at 1000 rpm for 4 hours. To get the anticipated pH level range (7~8), dilute HCL was added drop by drop until the mixture solution and stirred at 1000 rpm for 3 hours. The white gelatinous precipitate formed was filtered using filter paper. The precipitate was washed with distilled water several times until the pH value was approximately equal to 7 and then dried at 100 ºC for 24 hours. Finally, dried powders were calcined at 100 ºC intervals from 500 ºC to 900 ºC from room temperature in air for 6 hours to obtain spinal structure. The final samples were kept in a dry place to avoid moisture. The structural properties of all samples were characterized by XRD. Figure 1 shows the block diagram of the preparation of zinc stannate nanopowders and fibers.

Fabrication of Electrospun Zinc Stannate Nanofibers

Firstly, the polymer solution is made to obtain the nanofibers. The solution used to produce nanofibers was prepared with PVA. Fibers were produced using five types of Zinc Stannate nanopowder at different temperatures. Zinc Stannate nanopowder and solution are mixed and added to the beaker and then stirred with a magnetic stirrer. The mixture was first heated at 100 with constant stirring until a transparent homogeneous polymer solution was formed. The electrospun Zn_2SnO_4/PVA nanofiber membranes were prepared using the electrospinning system. Then it was allowed to cool down to room temperature and was transferred to a syringe pump connected to a needle. A high voltage of 2.5 kV was applied between the tip of the needle and the grounded drum collector which were fixed to be 4 cm apart. The PVA nanofibers were deposited onto a glass substrate which was attached to the drum collector by an aluminum foil. The nanofiber membrane deposited on the glass substrate, whether or not it is a fiber was examined with SEM.

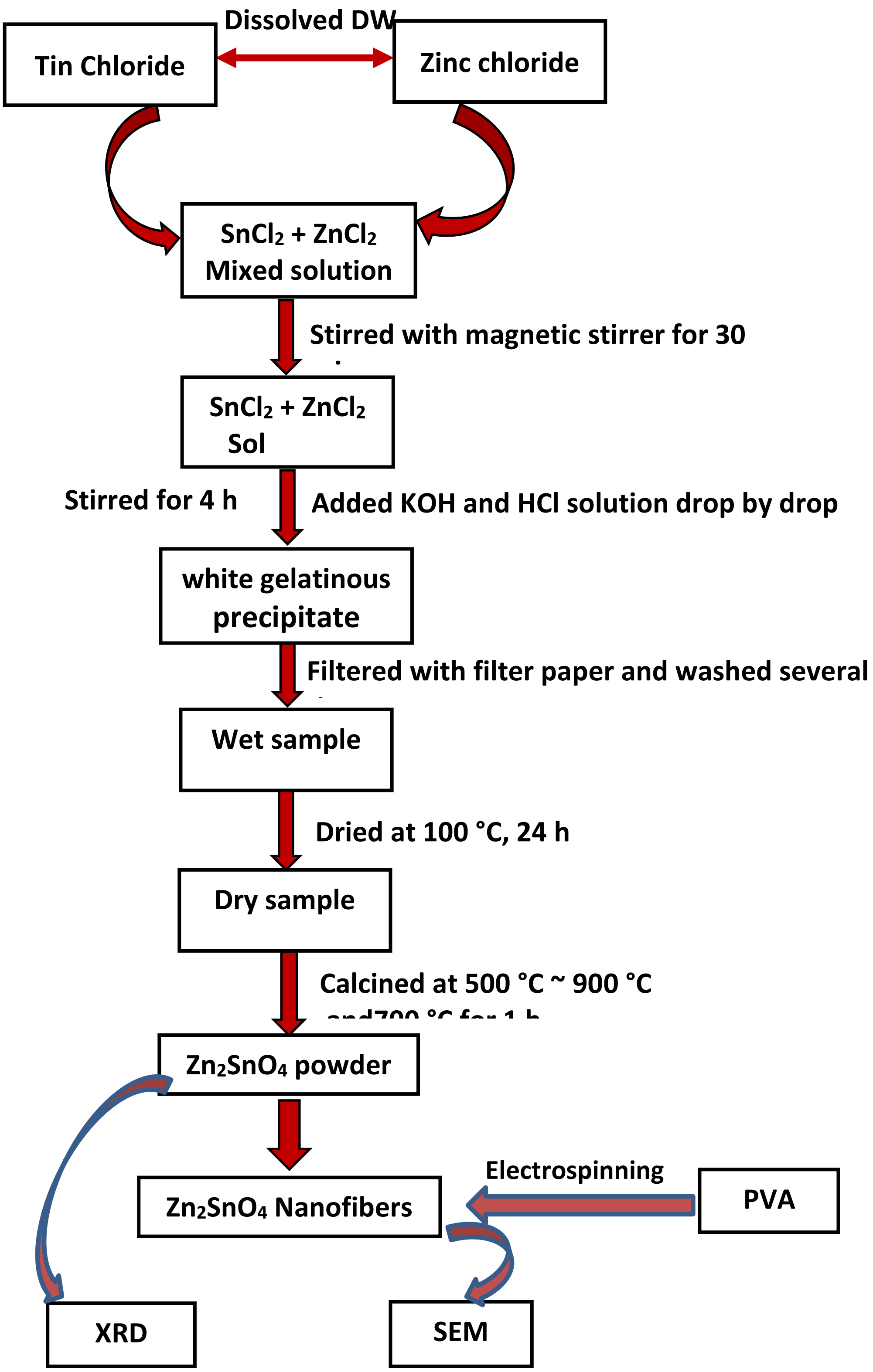

Figure 1 The Block Diagram of Preparation of Zinc Stannate Nanofibers

Results and Discussions

Characterization Techniques

The nanopowder and nanofiber synthesis of zinc stannate was characterized by XRD and SEM for structural, and morphological properties.

XRD Analysis of Zinc Stannate Nanopowder

X-ray diffraction is a powerful technique for investigating the structure of crystalline materials. To examine the crystal structure and phase formation of zinc stannate (Zn_2SnO_4) nanopowders at 500 ºC, 600 ºC, 700 ºC, 800 ºC, and 900 ºC was performed using monochromatic CuK_α radiation (λ = 1.54056 Å) operated at 40 kV (tube voltage) and 30 mA (tube current). The sample was scanned from 10˚ to 80˚ in diffraction angle, 2θ with a step-size of 0.01˚. Figure 2 shows the comparison of the XRD spectrum of zinc stannate (Zn_2SnO_4) nanopowders with tin chloride ($SnCl_2$) and zinc chloride ($ZnCl_2$) at five different temperatures of zinc stannate nanopowders. On the XRD spectrum, the (110), (311), and (440) peaks were sharply observed. The upper side of the XRD profile represented the observed profile while the lower side indicated the standard JCPDS (Joint Committee on Powder Diffraction Standards) library file. The dominant peaks were compared to the data from the library (or) standard file (pdf card no. 00-024-1470 Zn_2SnO_4). They were well-matched with the standard library profiles. The dominant peaks were well matched with the library (or) standard file of zinc stannate (Zn_2SnO_4). X-ray diffraction (XRD) demonstrated the cubic perovskite structure of the zinc stannate (Zn_2SnO_4) nanopowders. The average crystallite size of zinc stannate (Zn_2SnO_4) nanopowders at 500 ºC, 600 ºC, 700 ºC, 800 ºC, and 900 ºC were described in Table 1. The calculated microstrain and dislocation density were listed in Table 2. Interpretations from XRD show that the average crystallite size of 500 °C, 600 °C, 700 °C, 800 °C and 900 °C is 37.65 nm, 37.96 nm, 38.17 nm, 42.41 nm, and 48.23 nm respectively. The crystallite size of the particle improved by increasing the calcined temperature. The crystalline size was determined by the Debye-Scherrer formula,

$$G = \frac{0.899\lambda}{B_{(rad)} \times \cos\theta_B}$$

Where G = Crystallite size (Å)

λ = Wavelength to compute d-spacing (λ = 1.54056 Å)

B = Full Width at Half Maximum

θ_B = Bragg angle (deg)

Table 1 Structural properties of Zinc Stannate Nanoparticles at different temperatures

Temperature	500 ºC	600 ºC	700 ºC	800 ºC	900 ºC
Average Crystallite size G(nm)	37.65	37.96	38.17	42.41	48.23

Table 2 Dislocation Density and Microstrain of Zinc Stannate Nanoparticles at different temperatures

Temperature	500 ºC	600 ºC	700 ºC	800 ºC	900 ºC
Average Dislocation Density δ (nm)$^{-2}$	0.0009	0.0007	0.0007	0.0006	0.0004
Average Microstrain (ε)	0.1744	0.1623	0.1647	0.1478	0.1284

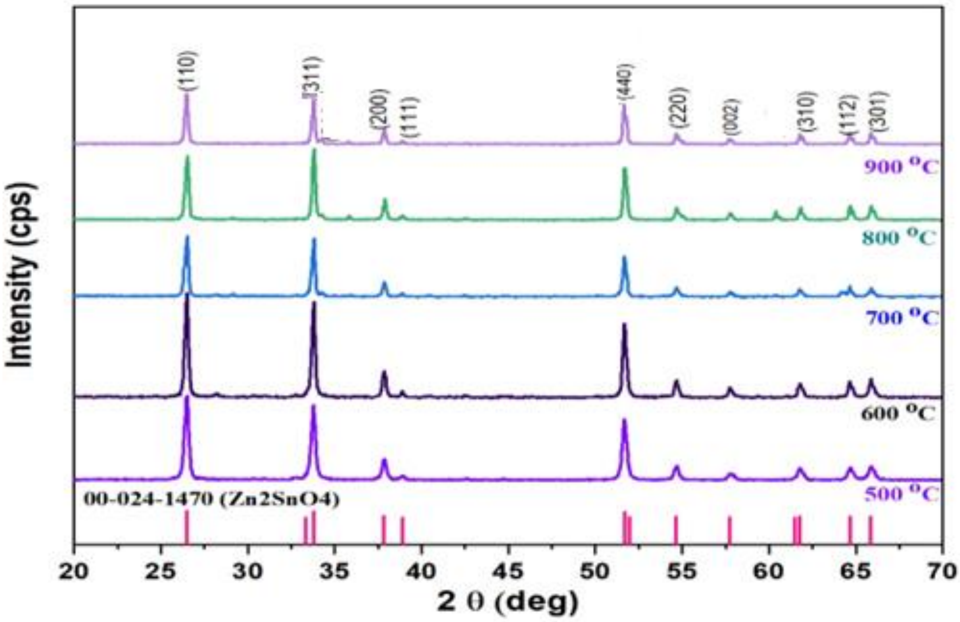

Figure 2 Compare of XRD spectra of Zinc Stannate nanopowder at (500 °C~900 °C)

SEM Analysis of Zinc Stannate Nanofibers

The electrospun PVA/Zn_2SnO_4 composite fibers on the FTO glass substrate were carried out to examine by SEM images. To study morphology and nanostructural properties of fabricated zinc stannate nanofibers are depicted in Figure 3 (a-e). The as-spun composite nanofibers appeared quite smooth and each nanofiber was quite uniform in cross-section. These nanofibers were found in the formation of aligned and web structures. The diameters of nanofibers were 0.27 µm (~270 nm) for 500 °C, 0.21 µm (~210 nm) for 600 °C, 0.20 µm (~200 nm) for 700 °C, 0.17 µm (~170 nm) for 800 °C and 0.13 µm (~130 nm) for 900 °C respectively. In Figures 3(a) and 3(d), the morphologies of fibers were smooth, uniform, and observed. For the images of figures 3(b), 3(c), and 3(e), the fibers were slightly rough, non-uniform, and found to be web-shaped. According to these results, the electrospun Zn_2SnO_4 nanofibers were successfully deposited on an FTO substrate for nanofiber-based photoanode in DSSC applications.

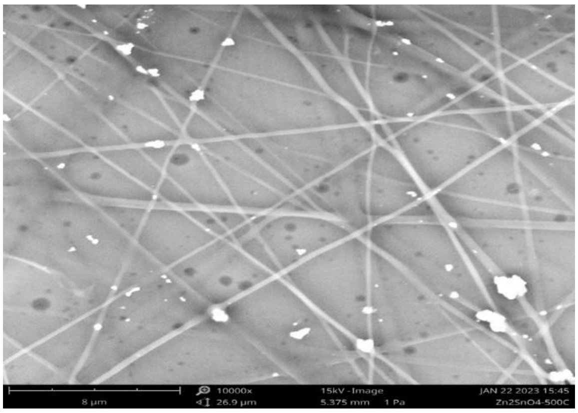

Figure 3(a) Zinc Stannate nanofibers at 500 °C (0.27 µm)

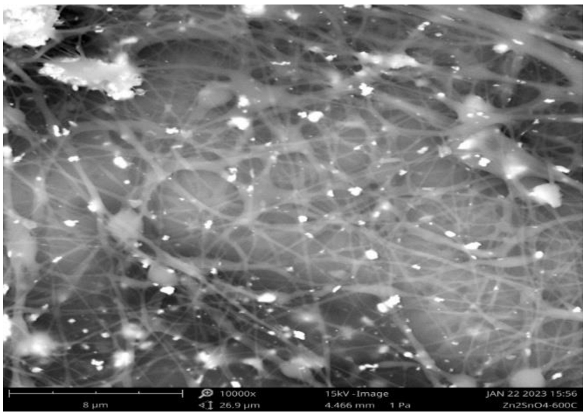

Figure 3(b) Zinc Stannate nanofibers at 600 °C (0.21 µm)

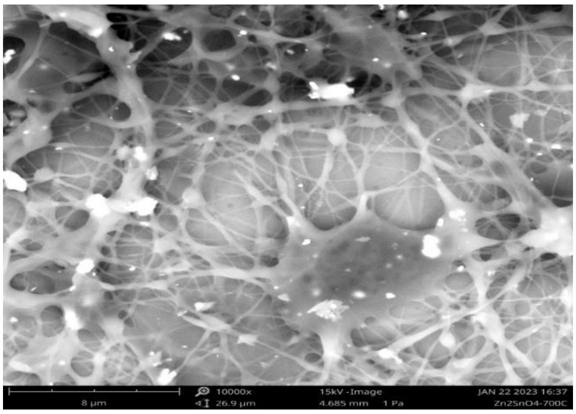

Figure 3(c) Zinc Stannate nanofibers at 700 °C (0.20 µm)

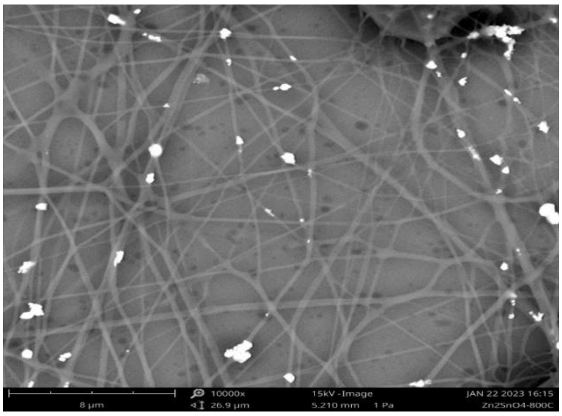

Figure 3(d) Zinc Stannate nanofibers at 800 °C (0.17 µm)

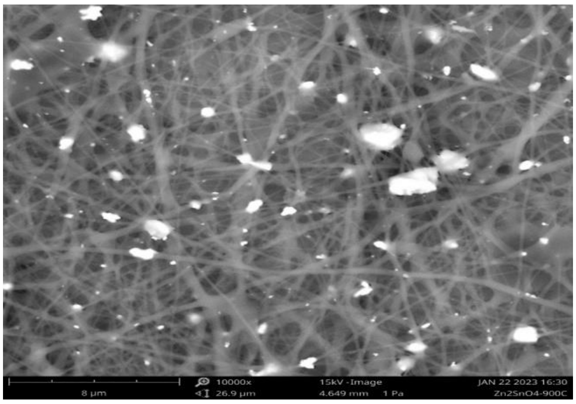

Figure 3(e) Zinc Stannate nanofibers at 900 °C (0.13 µm)

Conclusion

Zinc stannate (Zn_2SnO_4) nanoparticles were firstly prepared by sol-gel technique. Then, the synthesized) powders were calcined at five different temperatures. XRD analysis showed that nanopowders in the fabricated zinc stannate at 500 ºC, 600 ºC, 700 ºC, 800 ºC, and 900 ºC were crystallized in the cubic structure and their average crystallite sizes were observed to be 37.65 nm, 37.96 nm, 38.17 nm, 42.41 nm, and 48.23 nm respectively. From SEM analysis, the surfaces of zinc stannate nanofibers seemed to be more fiber shapes, web nature of fibers, definitely sharp and uniform distribution at 800 ºC than other temperatures. As a result, it was concluded that the average grain size of the zinc stannate powders varied with annealing temperatures. For the images of SEM, the fibers were slightly rough, non-uniform, and found to be web-shaped. The lack of clarity in the image of SEM is due to the need for homogeneity during the experiment, it will be having to do again. These were characterized by XRD and SEM techniques to investigate the structural and surface morphological properties of the samples and also revealed that it was influenced by the temperatures.

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