Chapter 3

Sol-Gel Process and Engineering Nanostructure

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Additional information is available at the end of the chapter

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Abstract

The production of ceramic nanostructures and engineering of their structure are the goals of the high-tech industry. Researchers prefer the sol-gel route to control the material at the atomic scale among other methods. In this chapter, we describe the production of ceramic nanostructures in different forms such as film, fiber, glass, and powder. We also discuss about microstructures and properties of these ceramic materials and the relationship between them.

Keywords: films, fibers, powder, sol-gel

1. Why engineering nanostructure

Economic necessities, scientific opportunities, and minimization have led to the development of nanotechnology and engineering nanostructure. A key aspiration of nanotechnology is to demonstrate the proposition that as things become small, often, they become differently interesting and useful and valuable structures.

At the atom and molecule scale, behaviors of atoms and molecules are only explicable on the basis of quantum mechanics. For the most part, the requirements of engineering nanostructure will necessitate that these syntheses generate highly homogeneous (both structurally and functionally) nanostructures. The polydispersity that characterizes most syntheses of colloids, for example, without purification, it's impossible to make uniform crystallization [1–5].

2. Microstructure of ceramics

There is a solid connection between the physical properties of ceramics, process, and their microstructure. Subsequently, the significance of the investigation of the microstructure is clear in ceramic research [6]. Materials science is the examination of the relationship among processing, structure, properties, and execution of materials (**Figure 1**).

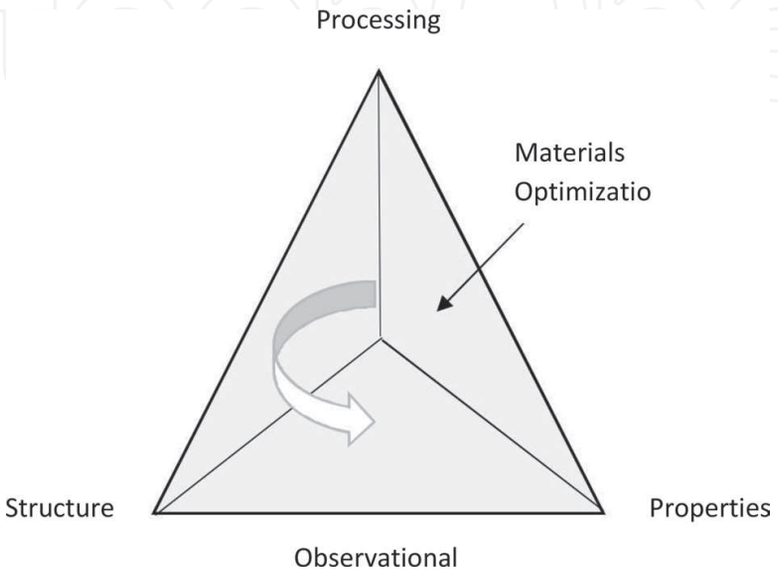


Figure 1. Relationship among processing, structure, and the properties.

3. Evaluation of the microstructure in ceramics

The microstructure and the subsequent properties of ceramics are not static in behavior. They might be changed by outer factors, for example, force and temperature. In the event that the

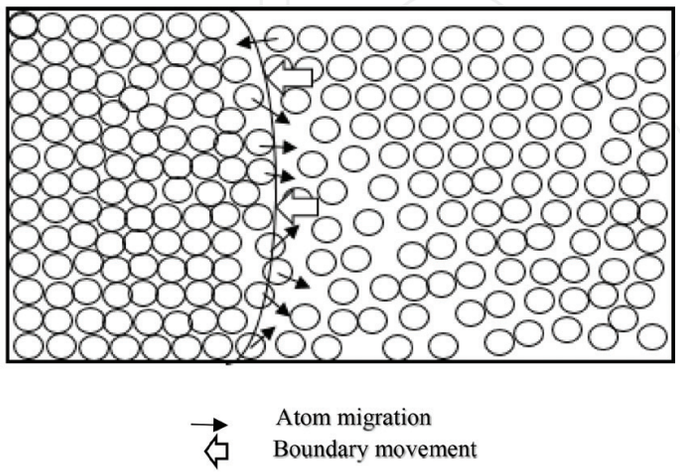


Figure 2. Schematic view of grain growth, showing interdiffusion of the atoms across the boundary. The boundary movement is toward the center of curvature, arising from the stability of the grains.

temperature is high in order to permit huge atom movements, the normal grain size of the ceramics will increase with time. The main impetus for grain growth is the free energy released as the atoms move over the boundary from the convex surface to the concave surface where the atoms end up noticeably planned with the bigger number of neighbors at balance atom spacing. Subsequently, the boundary moves toward the focal point of ebb and flow, and the bigger grains will develop to the detriment of the littler grains, as is shown in **Figure 2**. This is valid in both single-stage microstructures and polyphase microstructures. The net impact is less boundary territory per unit volume [7].

4. Methods of preparation of ceramics in the commercial stage

During the last decade, a wide number of synthesis methods have been developed for the preparation of ceramic powders; the main method is divided into two parts:

4.1. Solid-state reaction method

Industrial production is frequently based on solid-state reactions. But, solid-state reaction processes need high calcination temperature; this requirement leads to many disadvantages of the ceramic powders such as large particle size, wide size distribution, and high degree of particle agglomeration, which generally limits the ability to fabricate reliable electronic components and minimization.

Although this method can be improve with influence mechanochemical process on initial powder and sintering properties but impurities during process milling can be effected to ceramic properties.

4.2. Chemistry-based methods

Different chemistry-based routes have been proposed to produce high-purity ceramic fine powders at low temperatures. These include sol-gel processing, hydrothermal method, spray pyrolysis, oxalate route, microwave heating, microemulsion process, polymeric precursor method, etc. [8].

5. Sol-gel route

The sol-gel processing route was widely studied, because it is very effective in producing ceramic powders with high purity by using a purified precursor. Other advantages of the sol-gel route are good uniformity and a high homogeneous multicomponent system at relatively low temperatures, controllable kinetics of different chemical reactions such as hydrolysis-condensation and nucleation and growth of primary colloidal particles to obtain a microstructure with a special size and size distribution. Also, this route allows to control all of the processes to synthesize tailor-made materials, and homogeneity can be controlled until the atomic scale [9–11].

6. Preparation of ceramics in nanoparticle and fabrication nanosystem

The utilization of nanostructure materials is not another advancement. During the fourth century AD, Romans were utilizing nanosized metal to enhance cups and glasses [12].

Presently, old and novel techniques are utilized to synthesize nanoparticles in an industrial portion. These include sol-gel and chemical wet strategies, flame and spray pyrolysis, and synthetic vapor systems.

As a rule, maximum synthesis techniques and fabrication nanosystem can be divided into two important procedures: "top-down" (microcontact printing and photolithography) and "bottom-up" (self-assembly—organic synthesis) and their combinations. "Top-down" strategies start with a material or a group of macroscopic materials and utilize conventional workshops or microfabrication techniques in which outside controlled apparatuses are utilized for cutting, milling, and shaping materials into the favored form and order, while "bottom-up" approach strategies start with the plan and amalgamation of particles that can self-assemble or self-organize into mesoscale and higher full-scale structures. Bottom-up strategies are utilized to gather atomic and molecular segments into a sorted out surface structure through the natural procedures in the control framework [13].

7. Self-assembly

Self-assembly is one of the phenomena wherein components of all kinds, exemplified by atoms and molecules, colloids, and polymers, have the ability to assemble themselves to form a larger functional unit. It is the key rule that can produce a structure and arrange it from the atomic scale to a huge scale. Finally, with spontaneous organization, a higher level of steady structure is achieved with minimal energy level. Methods and techniques for self-assembly include forces and interactions; some forces used include covalent bonds (chemical bonding), van der Waals interactions, electrostatic interactions, hydrogen bonding, magnetic force bonding, hydrophobic interactions, electrical force, and gravity.

Self-assembly between the atomic scale and the nanoscale with the sol-gel method is possible with control, nucleation, coagulation, and grain growth during the sintering process with control parameters such as temperature, rate of heating, soaking time, and atmosphere of interaction. So, we need to know about some techniques of molecular synthesis, colloid chemistry, and polymer

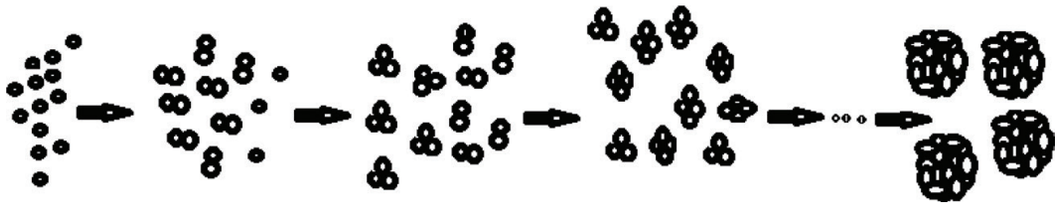


Figure 3. Schematic bottom-up and dynamic assembly of grain during the synthesis process.

science. Self-assembly reflects self-similarity that information coded (such as shape, surface properties, charge, polarizability, magnetic dipole, mass, etc.) in individual components; these characteristics can be determined with fractal dimension and self-similarity according to **Figure 3** [14].

8. Engineering nanostructure with the control grain growth process

Initially, we will define a grain growth concept and then evaluate the grain growth of ceramics, which is a combination of natural growth and self-assembly during growth. We then introduce a new tool that examines this complex phenomenon, which in the future will be able to control the reaction without human intervention and complete intelligence.

9. Grain growth nanostructure

Discovering the connection between the microstructure and macroscopic performance is useful for the improvement and utilization of ceramic materials. Concentrate the grain growth kinetic which has close connection with the assessment of ceramic microstructure. Research on grain growth is of rising interest nowadays and has attracted the attention of several researchers of various disciplines. Nanostructured (NS) materials have a large amount of stored energy due to their large grain boundary area and thus tend to be unstable with respect to grain growth during the sintering process. This problem usually is limited to sintering of NS ceramics at high temperatures. Particularly in industrial applications, how to suppress the grain growth of nanocrystalline materials and how to hold their excellent properties appear to be extremely important [15].

One of the fundamental objectives in sintering nanoparticles is to get dense compacts with held grain sizes in different forms. Hence, understanding subtle elements of the phenomenon of grain growth and the parameters influencing it is indispensable for an effective processing [16].

Ceramics are characterized as an artwork as well as a science of making and utilizing strong articles that have as their basic segment and are made in expansive part out of inorganic nonmetallic material. Sintering is an assembling system that has existed for delivering powder metallurgy parts and ceramic segments; amid the standard preparation of ceramics, powders are compacted and after that sintered at a temperature adequate to create helpful properties. Amid the way forward toward sintering, we should be worried about recrystallization and grain growth and, furthermore, the changing size and state of grains and pores [17].

10. Normal grain growth and kinetic exponent

During sintering of nanograins of ceramics, the normal size increases because of coarsening. The established marvel for depicting grain growth is called Ostwald ripening; in other words, expansive grains develop to the detriment of little grains that break up, prompting a stepwise increment of the normal size each time a little grain vanishes. In view of the customary mean-field estimation, the main thrust for grain growth is given by

$$\frac{\Delta G_m}{v_m} = 2\delta_p\left(\frac{1}{r_c} - \frac{1}{r}\right) \quad (1)$$

where is the molar volume, the critical radius and the average interfacial energy of the particle, Grains bigger than will develop and littler grains will shrink. Grains having the critical size in this way are in an unstable equilibrium with the matrix.

Ostwald ripening was considered in the traditional investigation exhibited by Lifshitz, Slyozov, and Wagner (the LSW hypothesis). The hypothesis proposes a stationary particle size distribution with a normal size expanding with time. The essential presumption of the LSW hypothesis is that the growth rate is relative to the driving force; in other words, the growth rate diminishes as the grain growth proceeds since the accessible surface energy diminishes amid the procedure.

Boundary movement is impacted by grain size, temperature, and impurities. Smaller grain sizes give a more noteworthy driving force to atom movement across the boundary, which can be spoken to by the following articulation [18]:

$$\frac{dD}{dt} = k/D^m \quad (2)$$

where D is the grain diameter and k and m are the constants. Some trial information demonstrates their qualities that are near solidarity. Accordingly, Eq. (2) disentangles to

$$D^{2-} D_0^2 = 2kt \quad (3)$$

This is a parabolic grain growth law. Thus, the adjustment in the cross-sectional zone of the grain is relative to time, or if the underlying size is thought to be zero, the diameter across increases with the square root of time. Moreover, the estimation of k is typically an exponential capacity of temperature in which k mirrors the activation energy for the atom movements.

11. Abnormal grain growth

Hypotheses of abnormal grain growth (AGG) treat this fascinating marvel regarding the relative grain size, or grain range, of the abnormal grains. Abnormal grain growth is the point at which few of the grains grow all the more definitely contrasting with the encompassing grains amid the sintering procedure. This growth is frequently seen in frameworks having faceted grains. A faceted grain has a particular interface and an anisotropic surface energy, while a circular grain has a harsh interface and an isotropic surface energy. Typically, grain growth of round grains is diffusion controlled and can be portrayed with the LSW hypothesis [19].

Abnormal grain growth dissimilar to normal grain growth is described by the exorbitant development of a moderately modest number of grains, while the rest remain unaltered until the point when they are expended. Because of its temperament, this marvel has been likewise called “grain coarsening,” “exaggerated grain growth,” “discontinuous grain growth,” and furthermore “secondary recrystallization” [20].

12. Classification of nanostructure with dimension

Nanomaterials could have one, two alternately, and three dimensions at the nanoscale.

One-dimensional nanomaterials include layer, multiple layers, thin films, platelets, and also surface coatings. They have been created what's more utilized for decades, especially in the electronic commercial enterprises.

Two-dimensional nanomaterials include nanowires, nanofibers committed starting with an assortment about elements, nanotubes also a subset about this assembly for carbon nanotubes.

Three-dimensional nanomaterials would know as nanoparticles also incorporate precipitates, colloids Furthermore quantum dots (tiny particles from claiming semiconductor materials), and Furthermore Nano-crystalline materials [21].

13. Sol-gel route for production of nanostructure ABO_3

ABO_3 with nanocrystal grains was synthesized by the sol-gel method. For ABO_3 fibers, same layer of ABO_3, acetate of A element, (A $(CH_3COO)_2$), and organic form of element of B same tetrabutyltitanate (B $(OC_4H_9)_4$) for film, fiber or powder were used as main raw reagents, and acetic acid (CH_3COOH) and ethyl alcohol as solvents. **Figure 4** shows the preparation process of nanostructured ABO_3 fibers, film, and powder by the sol-gel route.

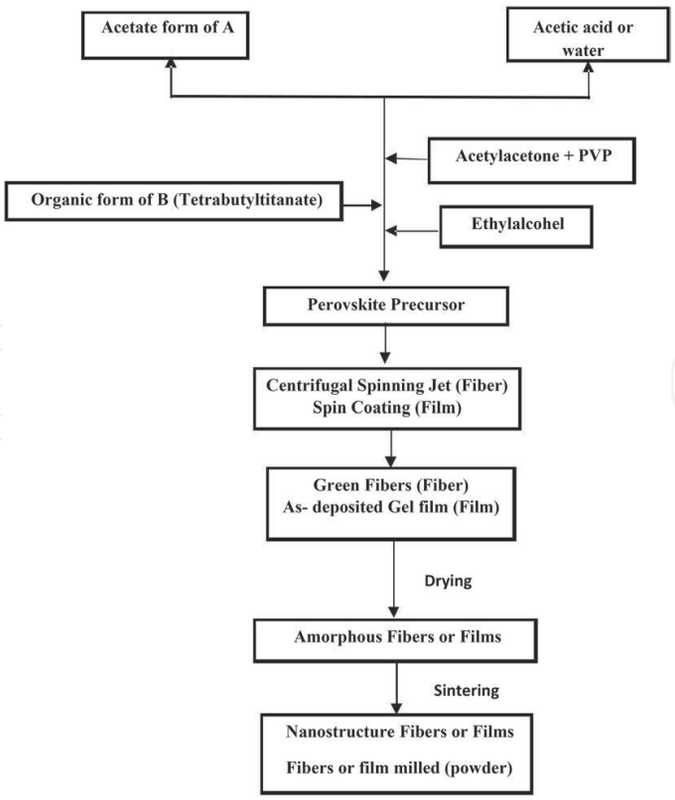
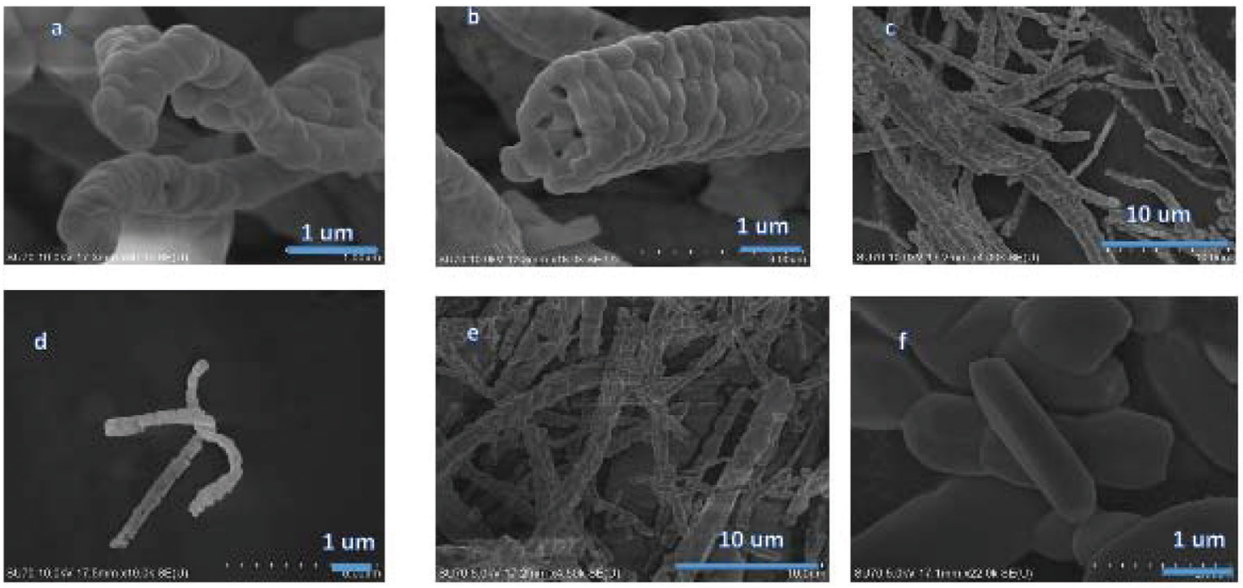


Figure 4. The preparation process of nanostructured ABO_3 fibers, film, and powder by the sol-gel route (Habibollah Aminirastabi Method).

14. Centrifugal spinning with sol-gel solution for production of nanostructure ABO_3 fibers

Different processes are used for synthetizing ceramic nanostructures, such as electrospinning, hydrothermal methods, laser ablation, and chemical vapor deposition (CVD), among which the centrifugal spinning is a highly efficient fiber formation technique that excludes some of the disadvantages of other methods, such as complex processing parameters (e.g., reaction temperature and pressure), low yield, low efficiency, long duration, and costly equipment (e.g., high voltage, reaction chamber, and autoclave) and processes. Hence, this method is capable of increasing the yield, efficiency, and safety in the production process of nanomaterials. **Figure 5a** and **5b** shows fibers sintered at different temperatures [22].



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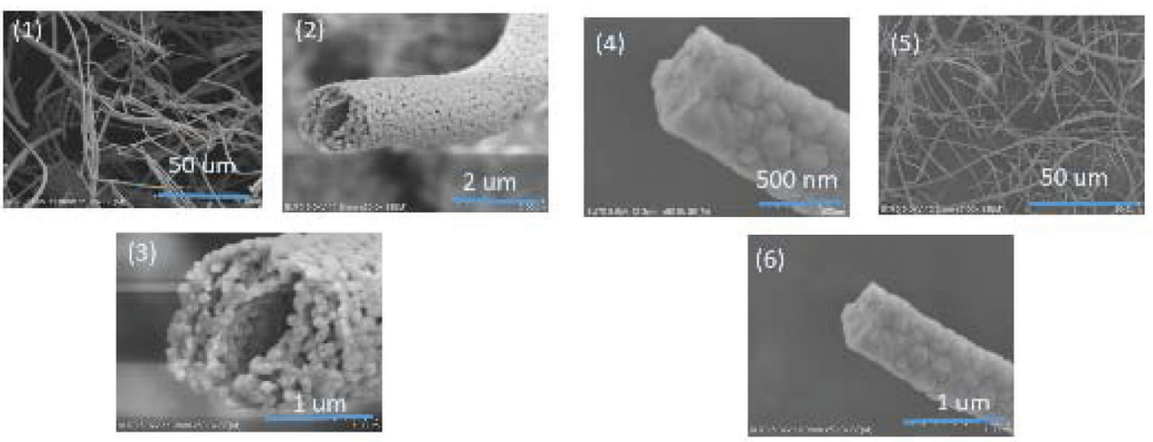

b

Figure 5. (a) SEM images of fibers sintered at 1100°C for 30 min: (a and b) $BaTiO_3$, (c and d) $SrTiO_3$, and (e and f) TiO_2. (b) (1–3) SEM micrographs of the $BaTiO_3$ tube sintered at 800^0 C for 2 hours and (4–6) SEM micrographs of TiO_2 rod sintered at 800^0 C for 2 hours.

15. Sol-gel route for production of nanostructure of ABO_3 layer and powder

Organic form of A element such as tetrabutyltitanate (Ti $(OC_4H_9)_4$) and acetate of B element were used as the main raw reagents, and acetic acid (CH_2COOH) and ethyl alcohol were used as solvents. Acetic solution of B element was mixed with polyvinylpyrrolidone dissolved in ethyl alcohol and acetyl acetate, and then tetrabutyltitanate was added. The mixture was stirred vigorously at room temperature for 1 hour to form the ABO_3 precursor. Then, the sol-gel solution was dried and calcined at 700°C for 10 min in different powders as shown in **Figures 6** and **7**.

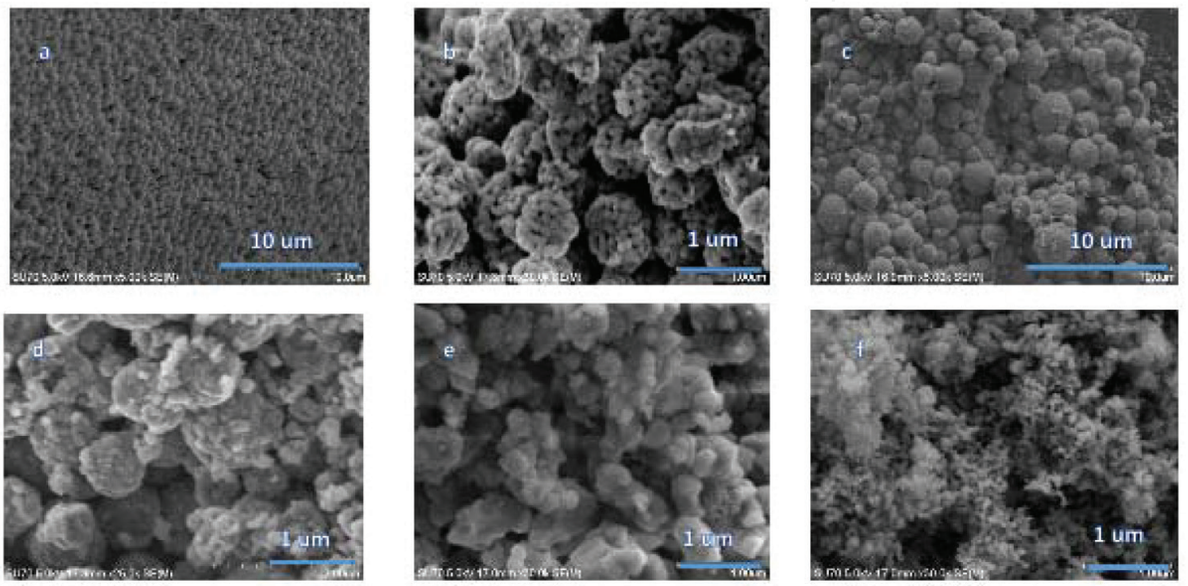

Figure 6. SEM images of powders sintered at 700°C for 10 min: (a and b) $CrTiO_3$, (c and d) $LiTiO_3$, (e) $SrTiO_3$, and (f) $BaTiO_3$.

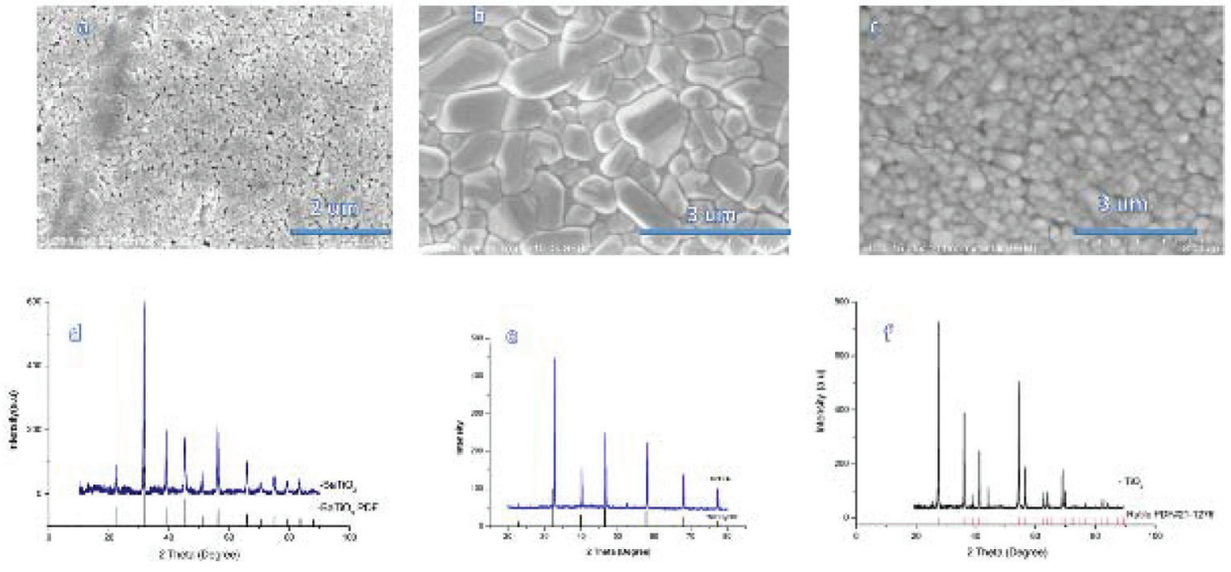

Figure 7. SEM images and XRD patterns of different layers sintered at different temperatures and soaking times: (a and d) $BaTiO_3$ 900°C for 120 min, (b and e) $SrTiO_3$ 1100°C for 120 min, and (c and f) TiO_2 900°C for 120 min.

16. Effect of additives on ABO_3 properties

Normally, ceramics with a perovskite structure has some defects such as point defects, vacancies, interstitial defects, line defects such as edge dislocation and screw dislocation, and plane defects such as grain boundary, tilt boundary, and twin boundary. The crystalline with structural defects that can be corrected by replacing atoms with an atomic radius equal to or smaller, and obtaining new properties with changing microstructure according **Figure 8**. For example, $BaTiO_3$ is doped with small amounts of strontium to improve properties such as permittivity two times more than that of $BaTiO_3$ and to decrease the temperature of sintering.

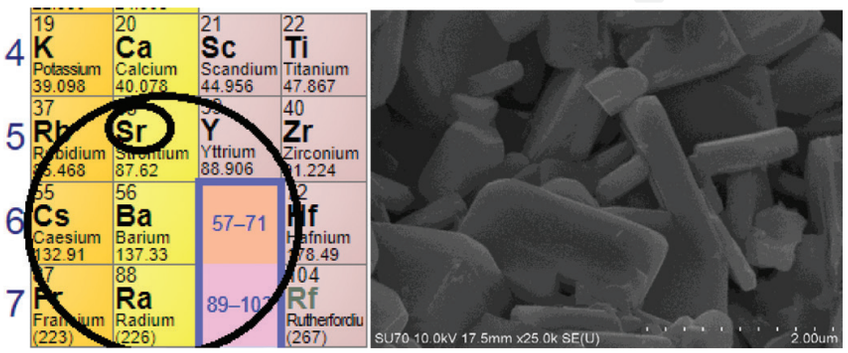

Figure 8. SEM micrograph of $(Ba_{95}Sr_5)$ TiO_3 with microstructure cubic grain.

17. Artificial intelligent tools for the grain growth process

Fractal analysis systems have the ability to make an image of different formats and analysis structures to find and calculate fractal dimension and coverage, from color, gray scale, binary, and 3D sliced (layer) images (**Figure 9**).

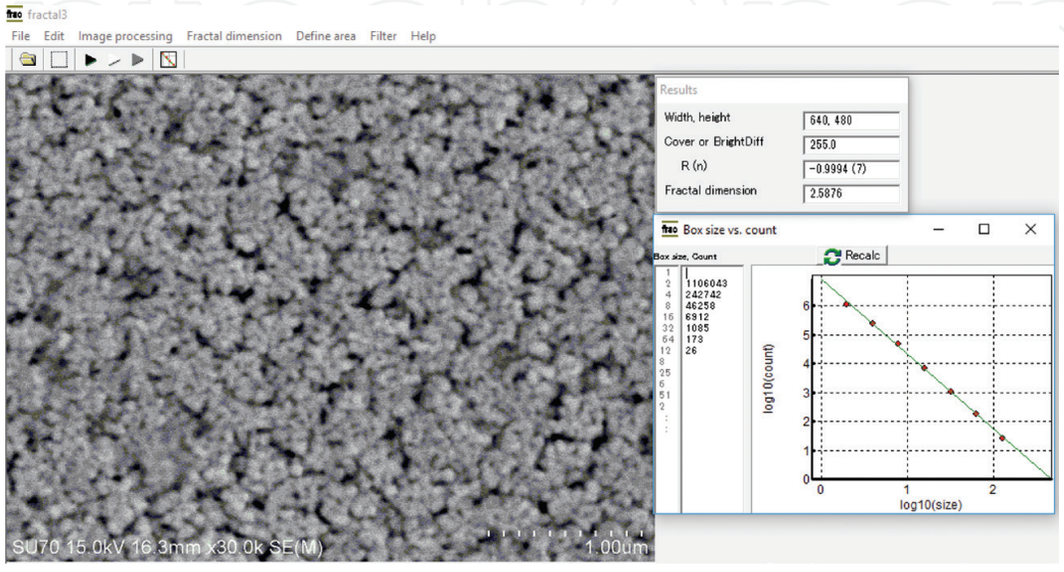

Figure 9. Image analysis of ceramic microstructure of BaTiO3 film sintered at 700°C for 100 minutes.

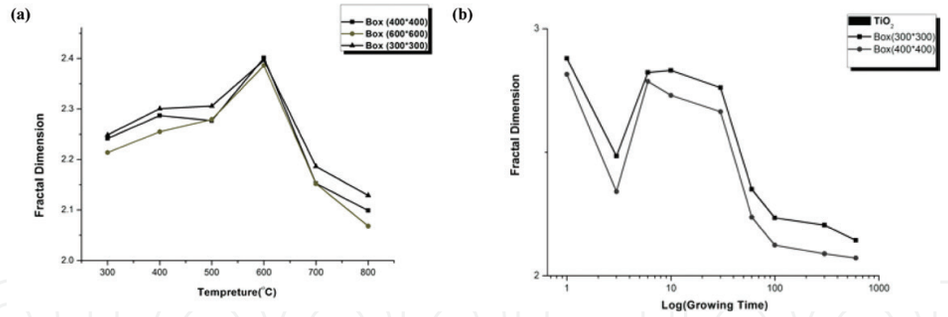

Figure 10. (a) variation of fractal dimension of the nanostructure at different temperatures for 2 hours. TiO_2 sintered at different socking times. (b) Nanostructure TiO_2 sintered at different socking times [24].

Fractal dimension can be calculated by the method of box-counting after preprocessing. The relationship between the size of the box and the count can be displayed with a plot graph. So, you can confirm whether the image is fractal or not by linearity. If limited sizes can be used for calculating fractal dimension, any of the count data can be deleted or edited to recalculate fractal dimension. The image can be filtered; isolated black points can be deleted and filtered for some cases of binary images with much noise. Fractal dimension of black area in many 3D sliced (layer) images (bmp) can be calculated [23] (**Figure 10**).

18. Conclusion

However, there are a number of factors that have influences on the physical properties of ceramics. The production of ceramic nanostructures and engineering of their structure to find single crystal properties are the goals of this research. The advantage of selecting the sol-gel route to produce nanostructures is that the size can be controlled from the atomic scale to the microscale. In this chapter, we describe the production of ceramic nanostructures in different forms such as film, fibers, and powder and some factors that influence grain growth such as temperature, soaking time, and rate of heating and combination of material during the sintering process and introduce tools to monitor the grain growth process, which will be intelligent during all the processes and work based on self-similarity.

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