Full Length Research Paper

Preparation of nanocrystalline strontium titanate (SrTiO₃) powder by sol-gel combustion method

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Nanocrystalline strontium titanate (SrTiO₃, ST) powders were prepared by sol-gel combustion method. The influence of fuel content ratio (ratio of citric acid (CA) and total metal nitrate (MN); Ra = CA:MN) and calcination temperature were investigated on the structure, morphology, and crystallite size by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results indicate that the Ra ratio of 3:1 is adequate for a good crystallization of pure perovskite phase after calcination by combining the washing process with nanometric crystallite size and porous microstructure. For the SrTiO₃ powder synthesized with Ra ratio = 3:1, the effect of calcination temperature was investigated, showing that the perovskite structure is optimum crystallized at 500°C, without secondary phase formation. The particle sizes increased with increasing Ra ratio and calcination temperature.

Key words: Sol-gel combustion method, strontium titanate and fuel content ratio, nanocrystalline powders.

INTRODUCTION

Strontium titanate (SrTiO₃, ST) with a perovskite-type structure is an important ceramic material having wide uses in the catalysis, sensors, actuators, electrooptical devices, random access memory devices, and multilayer capacitor (Ishikawa et al., 2008; George et al., 2009; Rangel-Hernandez et al., 2009; Li et al., 2010; Liu and Bai, 2011; Xian et al., 2011). Because ST have a lot of physical and chemical properties, such as, high thermal and chemical stability, low coefficient of thermal expansion, large dielectric constant, low dielectric loss, high nonlinear optical coefficient, it is widely accepted that the practical performances of product are strongly influenced by its phase, morphology, particle size, crystal defects, surface properties, etc., which ultimately depend on its preparation method and condition (Li et al., 2010; Liu and Bai, 2011; Xian et al., 2011).

Several synthesis techniques have been developed for the preparation of SrTiO₃ nanoparticles, such as solid-state reaction (Berbenni et al., 2001; Zhang et al., 2004), hydrothermal (Chen et al., 2000; Xu et al., 2006; Rangel-Hernandez et al., 2009), combustion (Poth et al., 2000a; Ishikawa et al., 2008), sol-gel (Xuewen et al., 2001; Cui et al., 2007), ultrasonic spray pyrolysis (Kim et al., 2002), coprecipitation (Patra et al., 2006), peroxide-Based route (Wanjun and Donghua, 2007), polymeric precursor method (Da Silva et al., 2011), solvothermal method (Wang et al., 2010; Bacha et al., 2011), molten salt method (Li et al., 2010), and sol-gel combustion method (Xue et al., 2007; Liu et al., 2008). Recently, sol-gel combustion method is widely used to prepare the nanomaterials with high impurity, better homogeneous, small grain size, and relatively low crystallization temperature than the conventional synthesis method, which is based on the sol-gel process and the subsequent combustion process. In the combustion process, the fuel that is an organic as citric acid (CA) is ignited to combust by the reaction itself and not by an external source. Thus, this method has the advantages of low synthesis temperature, rapid synthesis process, and nanocrystalline structure. However, the chemical synthesis processes have some disadvantages, including

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impurities to be easily introduced from solution. Thus, the combination of a subsequent washing process technique was applied to take out the disadvantage. This method does not only overcome it, but also achieve the low temperature and energy saving for comparison with increase in the time of calcinations or calcinations temperature.

Several works were reported in the field of $SrTiO_3$ powder preparation by sol-gel combustion method. Liu et al. (2008) synthesized nanocrystalline $SrTiO_3$ powder by sol-gel combustion method using CA as fuel in the range of 20 to 30 nm at low temperature of 400°C. They used the molar ratio of $Sr:Ti:CA:NO_3^-$ of 1:1:3:0.84, but did not investigate the effective of the different fuel content ratio. Xue et al. (2007) studied the preparation of nanocrystalline $(Sr, Pb)TiO_3$ by self-propagation combustion method that varied the mole ratio of glycine:$Sr(NO_3)_2$:$TiO(NO_3)_2$ as (1.5, 2.0, 2.5, 3.0):1:1. They also investigated on photocatalytic activity of it by adding the amount of $Pb(NO_3)_2$ to precursor solution. Also, Poth et al. (2000b) investigated the influence of reaction parameters like the amounts and ratios of oxidizing and reducing reactants and the ignition temperature which are prepared by sol-gel combustion method.

In past researches, the effects of fabrication parameters on the structure of $SrTiO_3$ nanopowders synthesized by sol-gel combustion method were not properly studied, so the aim of this research was to study the influence of fuel content ratio and calcination temperature on the structure, morphology, and crystallite size of $SrTiO_3$ powder prepared by the sol-gel combustion method.

MATERIALS AND METHODS

For the preparation of the precursor solution, all chemicals were of analytic grade and without further purification. The $SrTiO_3$ powders were synthesized by sol-gel combustion method using CA as chelated agent. For starting, $Ti(OH)_4$ was prepared from the hydrolysis of titanium(IV) chloride and titanyl nitrate ($TiO(NO_3)_2$) was obtained by dissolving $Ti(OH)_4$ in nitric acid. Firstly, CA and $Sr(NO_3)_2$ were dissolved by continuous stirring in deionized water to form a solution, according to the fuel content molar ratio, the ratio of CA and the total metal nitrate (MN) (Ra; Ra=CA:MN) of 1:1, 2:1 and 3:1 respectively. Next, the previous solution and $TiO(NO_3)_2$ solution were mixed together to form a transparent solution. After that the solution was heated at 80°C under vigorous stirring until a gel was formed, then the gel was dried in the electric oven as the as-product. Finally, the as-products were calcined at the temperature range between 500 and 800°C for 2 h with heating and cooling rate about 2°C min⁻¹. Additionally, the residue solid was washed with 1 mol/L HNO_3 aqueous solution and deionized water to remove the impurity (such as $SrCO_3$) and was dried in air at 100°C.

X-ray diffraction (XRD), using X'pert model of Phillips, was obtained to identify the phase present and their crystallite size, in a 2θ range from 10 to 60°, using Cu Kα radiation. The crystallite size of the calcined powders was obtained by X-ray line broadening method. The crystallite size of the calcined powders can be estimated by X-ray line broadening analysis according to the

Scherrer formula:

$$D_{XRD} = \frac{k\lambda}{\beta \cos \theta}$$

Where, λ is the X-ray wavelength (0.154056 nm); k is the constant (this work used about 0.9); θ is the diffraction angle of the major characteristic peak intensities for 110 peak and β is the full width at half maximum (FWHM) of the 110 peak (in radian). The relative amount of perovskite and impurity phase was determined by measuring the major XRD peak intensities of the perovskite (110) or I_p and impurity phase or I_{im}, as the following equation (Wongmaneerung et al., 2006):

$$\textbf{\textit{Perovskite phase (wt\%)}} = \left(\frac{I_p}{I_p + I_{im}} \right) \times 100$$

The microstructure and morphology study of the ST powder were investigated by a scanning electron microscopy (SEM) using JOEL Leo1455VP equipment.

RESULTS AND DISCUSSION

XRD patterns of the ST powder samples, prepared with different Ra ratios after calcination at 600°C for 2 h, were displayed as shown in Figure 1. Sample prepared with Ra ratio of 1:1 exhibited a mixture of phases, which were identified as predominant of ST and impurity phases ($SrCO_3$).

Sample prepared with Ra ratio of 2:1 presented an impurity phase in the phase formation, and ST is still poorly crystallized. XRD pattern of the sample synthesized with Ra ratio 3:1 shows a great improvement in the formation of ST phase; although, the $SrCO_3$ impurity phase still occurred, but it was reduced. For comparing the percentage of perovskite phase of ST powder with different Ra ratios, they show about 59.7, 47.8, and 73.6, respectively. The results of the percentage of perovskite phase showed the effective trend of the fuel content ratio for the good crystallization of perovskite phase after calcination. Higher Ra ratio presented high percentage of perovskite phase. Thus, it can be concluded that Ra ratio of 3:1 is the most favorable condition for synthesis of $SrTiO_3$.

Once the optimal value of the Ra ratio was defined for the synthesis of ST, we studied the influence of calcination temperature on phase formation. The ST powders prepared with Ra ratio of 3:1 was calcined at a temperature between 500 and 800°C for 2 h. XRD patterns of the samples calcined at different temperatures are shown in Figure 2.

After calcination at 500°C, the XRD patterns indicated those of the cubic form of ST and formations of impurity phases, which reveal the characteristic of $Sr(NO_3)_2$ and $SrCO_3$. As the calcination increases to 600°C, $Sr(NO_3)_2$ phases disappeared, although, the $SrCO_3$ phases still
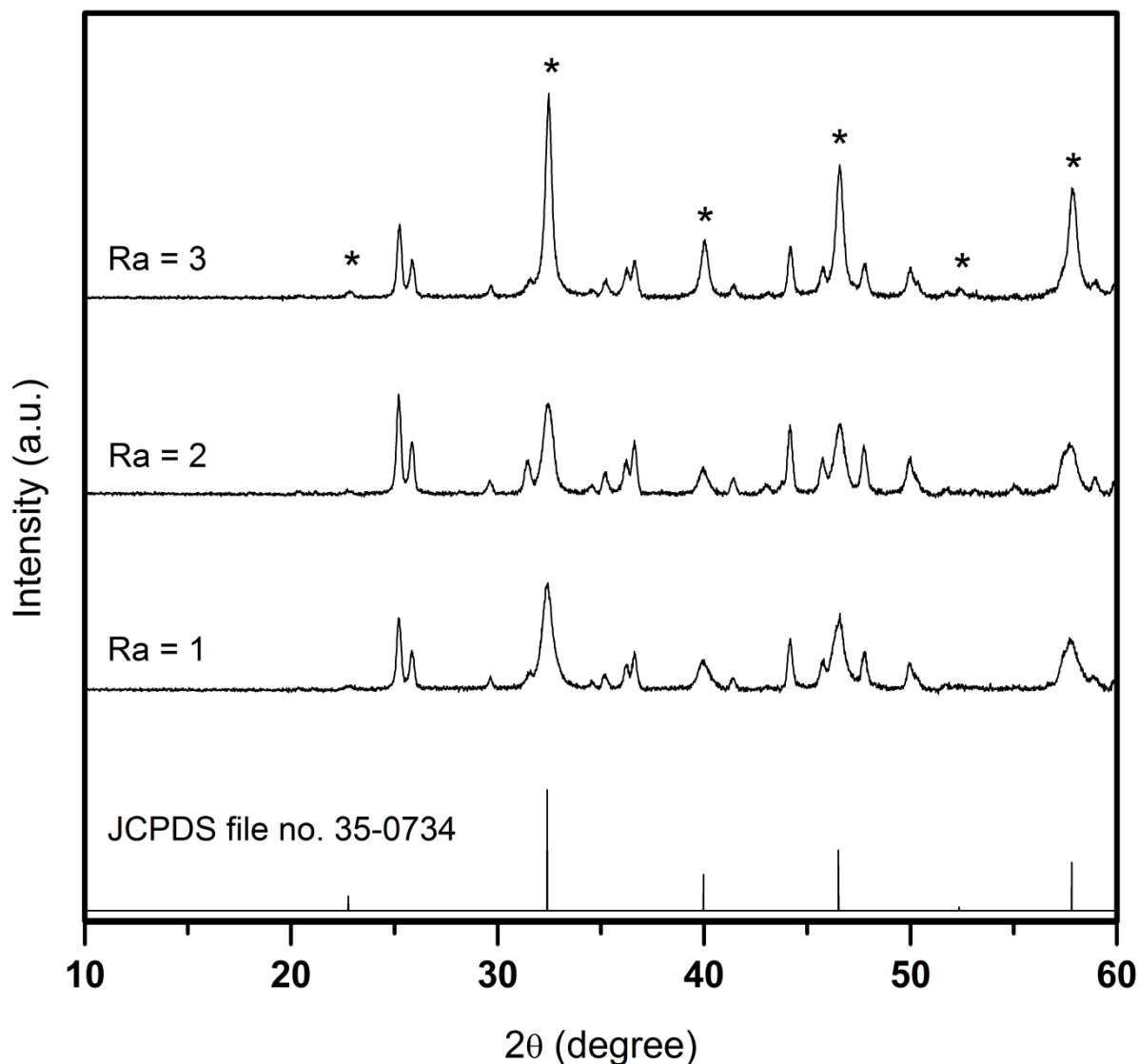
Figure 1. XRD patterns of SrTiO₃ powders prepared with Ra ratio of 1:1, 2:1, and 3:1 after calcination at 600°C for 2 h; (* SrTiO₃).

manifested and were obviously observed at XRD pattern until calcination at 800°C. However, peaks due to perovskite ST phase become sharper as the calcination temperature increases to 800°C. Perovskite ST phase can be formed gradually at higher calcination temperature; however, the impurity $SrCO_3$ phases occurred along with them. Thus, it can be summarized that trend of perovskite phase increases with the increase of calcination temperature.

The average crystallite sizes, the percentage of perovskite phase, and lattice parameters of ST powders after the washing process and calcination at different temperature are listed in Table 1. The average crystallite sizes with Ra ratio of 3:1 obtained in this study are in the nanometers (that is, about 24 nm). Thus, they presented the cubic structure with lattice parameters close to ST lattice parameters; a = 3.9050 Å, which is a good agreement with the reported XRD data in JCPDS file number 35-0734. However, the percentages of perovskite phase tended to increase with the increase of calcination temperature.

In addition, the technique with a subsequent washing process by HNO_3 solution was also attempted to remove the $SrCO_3$ impurity phase in all Ra ratio. The powders with lower Ra ratios showed that $SrCO_3$ impurities remained in the XRD results. However, powders prepared with Ra ratio of 3:1 at different temperature were completely obtained by this technique. Therefore, the result shows that the undesirable $SrCO_3$ impurity that occurred in the synthesis process can be eradicated. This
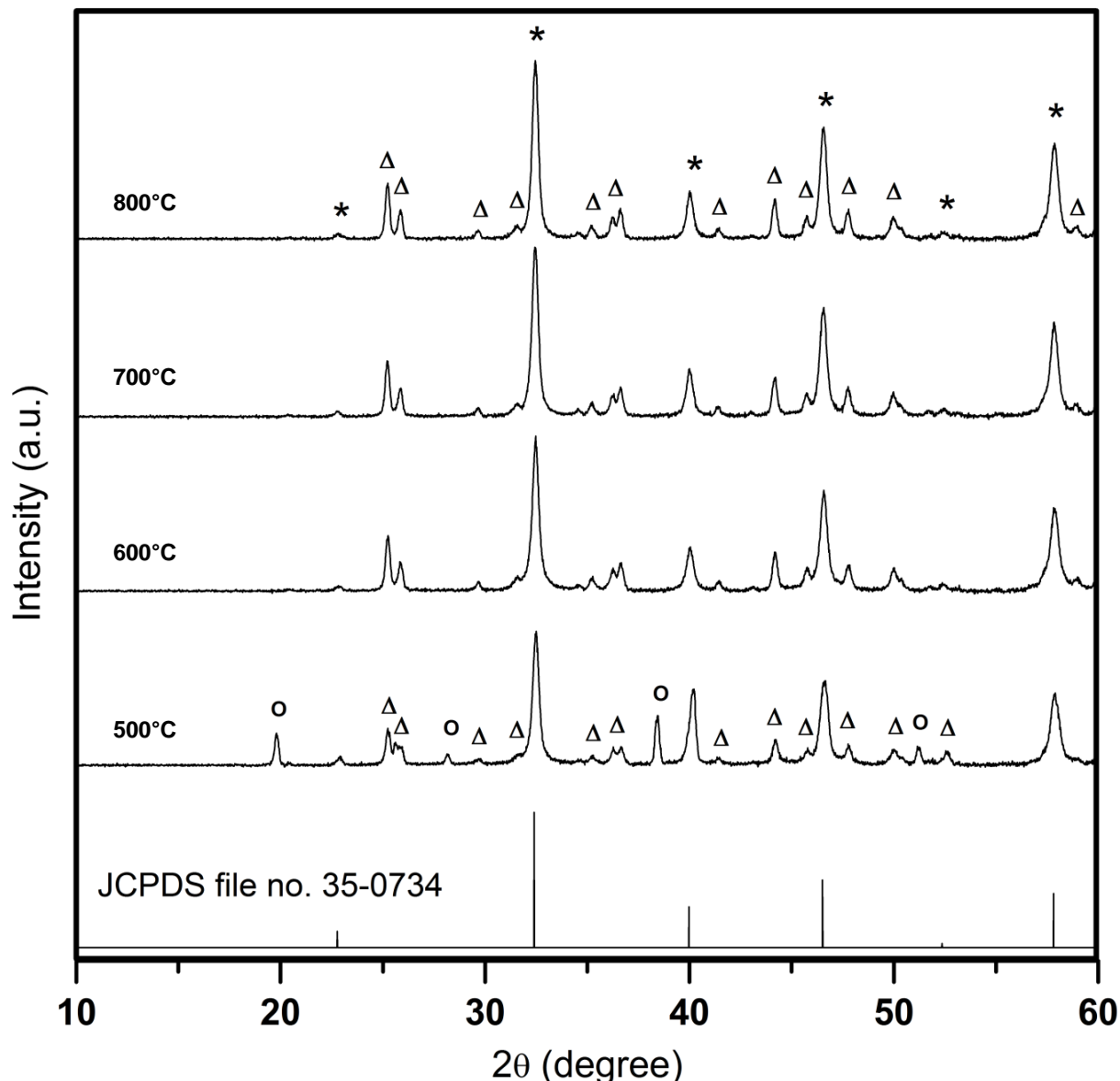
Figure 2. XRD patterns of SrTiO₃ powders prepared with Ra ratio of 3:1 after calcination at different temperature; (*SrTiO₃, °Sr(NO₃)₂, and ᐃSrCO₃).

impurity perfectly disappeared when the calcination temperature was 500°C as seen from the XRD pattern in Figure 3.

Figure 4 shows the microstructure of ST powders prepared with different Ra ratios and calcined at 700°C temperature. However, particles in both samples are nearly spherical in shape. The powder prepared with deficiency of fuel content (Ra ratio = 1:1) presented the formation of agglomerates of fine particles, with low porosity. The average particle sizes of ST powders with Ra ratio of 1:1 was estimated to be about 42 nm. There was small improvement in microstructure for the powder prepared when increasing Ra ratio, with a more loose and porous structure. The average particle sizes of

ST powders with Ra ratio of 3:1 was about 45 nm. Thus, it is demonstrated that Ra ratio has an influence on morphology of calcined powders within the agglomerated structure and particle size. By the way, the average particle sizes tended to increase with increase in calcination temperature and the particles agglomeration also appears to decrease with increase in fuel content ratio.

Conclusion

The SrTiO₃ nanopowders were successfully synthesized by sol-gel combustion method using CA, varying the CA

Table 1. Average crystallite size (D_{XRD}), percentage of perovskite phase, and lattice parameters of $SrTiO_3$ samples after washing process prepared with Ra ratio of 3:1 and calcined at different temperatures.

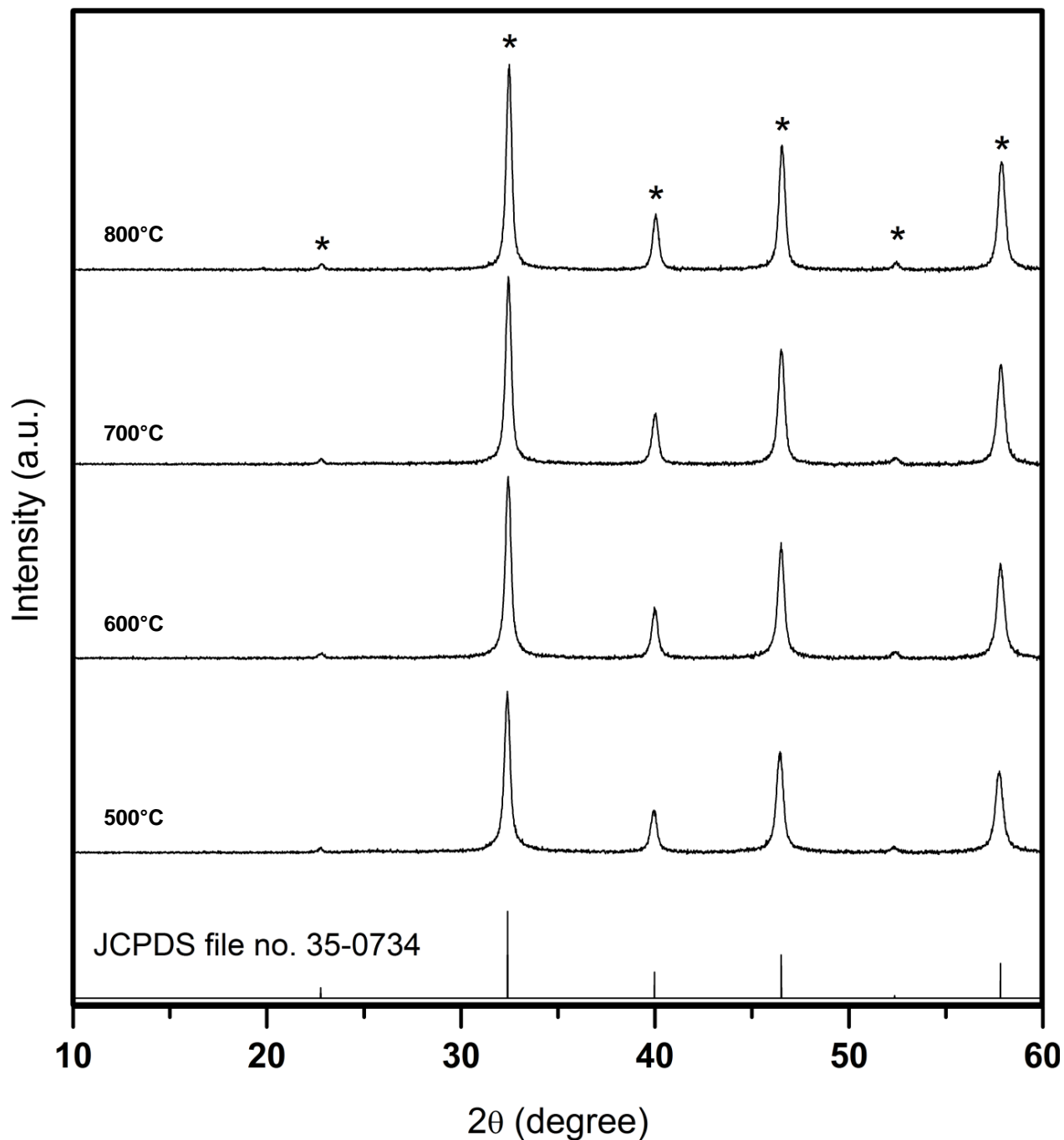| Calcined temperature (°C)	D_{XRD} (nm)	Perovskite phase (%)	Lattice parameters (Å)
500	23	100	3.9077
600	23	100	3.9029
700	24	100	3.9014
800	25	100	3.8988

Figure 3. XRD patterns of $SrTiO_3$ powders prepared with Ra ratio of 3:1 after calcination at different temperature, combined with a subsequent washing process.
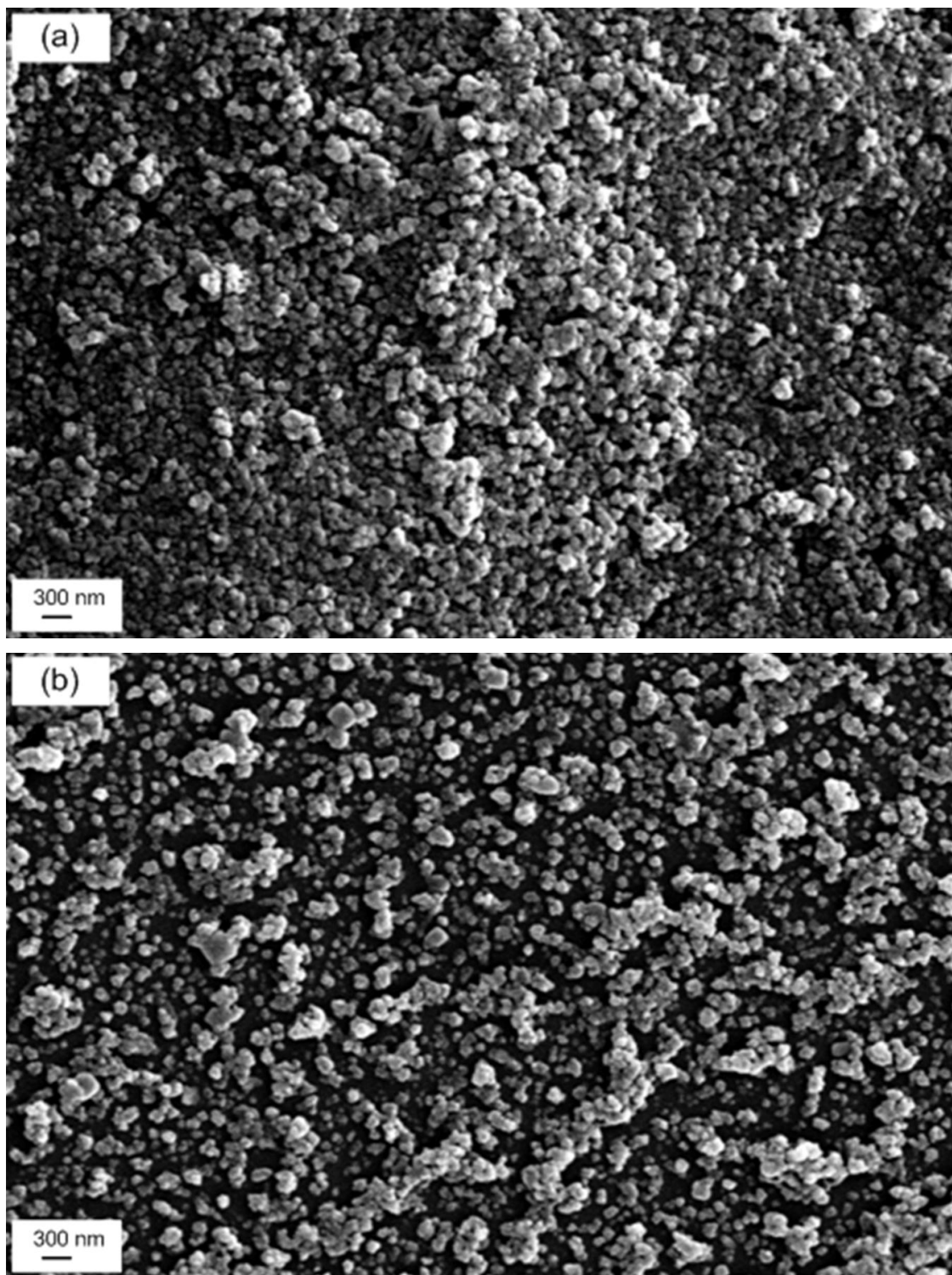
Figure 4. SEM micrographs of SrTiO$_3$ powders prepared with Ra ratio of 1:1 (a) and 3:1 (b) that calcined at temperature of 700°C.

content:total metal nitrate molar ratio and calcination temperature, combined with a subsequent washing process. The undesirable SrCO$_3$ impurity which appeared under certain experimental condition could be perfectly removed either by HNO$_3$ washing process. The important variables affecting the product quality of SrTiO$_3$ by sol-gel

combustion method include: The fuel content ratio and calcination temperature. The Ra ratio of 3:1 provided good effectiveness condition for the preparation of single phase nanocrystalline $SrTiO_3$. The average crystallite size of $SrTiO_3$ was affected in both Ra ratio and calcination temperature. The particle size increases with increase in Ra ratio and calcination temperature. The crystallite size was illustrated in range of nanometer.

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