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Preparation of nanocrystalline $SrTiO_3$ powder by sol–gel combustion method

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Abstract

In this research a sol–gel combustion route has been presented to synthesize strontium titanate ($SrTiO_3$:ST) nanocrystalline, using citric acid as fuel. The synthesis procedure was optimized by systematically varying the molar ratios of total metal nitrate to citric acid (MN:CA) from 1:1 to 1:3. The effect was investigated through XRD, SEM and TEM analysis. Analysis of XRD spectrum shows the complete of $SrTiO_3$ nanocrystalline, however, a minor phase of $SrCO_3$ impurity was found. Hence, an acid treatment process, with 1 mol/l HNO_3 solution and deionized water, was applied to remove the impurity. The results show that the appropriate condition to prepare the single phase nanocrystalline $SrTiO_3$ powders is MN:CA molar ratio of 1:3, coupled with an acid treatment process and at the lower calcination temperature of 500 °C. The particle size of powders was in nanometer ranges. The average crystallite size calculated from FWHM was about 23 nm. Morphology of powders was identified by SEM analysis. However, TEM estimated the average particle size about 7.5 nm after applying an acid treatment technique at 600 °C.
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1. Introduction

Strontium titanate ($SrTiO_3$, ST) with a perovskite-type structure is an important ceramic material having wide use in the catalysis, sensors, actuators, electrooptical devices, random access memory devices and multilayer capacitor [1–6]. $SrTiO_3$ have many property advantages, such as large dielectric constant, low dielectric loss, high thermal and chemical stability, etc. It is accepted that the practical performances of product are strongly influenced by its phase, morphology, particle size, crystal defects and surface properties, etc. which ultimately depend on its preparation method and preparation condition [3,4,6].

Several synthesis techniques have been developed and modified. Thus, various synthesis techniques have been used to fabricate $SrTiO_3$ powders such as solid-state reaction [7,8], hydrothermal method [9], combustion method [2], sol–gel method [10], ultrasonic spray pyrolysis [11], coprecipitation [12], peroxide-based route [13], polymeric precursor method [14], solvothermal method [5], molten salt method [3] and sol–gel combustion method [16]. Recently, sol–gel combustion method is popular for preparing nanomaterials with high purity, better homogeneous, small grain size and relatively low crystallization temperature than the conventional synthesis method. However, the chemical synthesis processes have some disadvantages including impurities easily introduced from solution. Thus, the combination of an acid treatment technique was applied to overcome the disadvantage. Many research have studied the combination of an acid treatment technique with main preparation methods such as solid phase grinding [17].

In the past, the effects of fabrication parameters on structure of $SrTiO_3$ nanopowders synthesized by sol–gel combustion method have not been studied sufficiently, so the aim of this research is to study the influence of the different fuel content and calcined temperature on the

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crystal structure, morphology and particle size of powders that are prepared by sol–gel combustion method. The effect of an acid treatment technique was investigated.

2. Experimental method

$Ti(OH)_4$ was prepared from the hydrolysis of $TiCl_4$ and $TiO(NO_3)_2$ was obtained by dissolving $Ti(OH)_4$ in nitric acid. Firstly, citric acid and $Sr(NO_3)_2$ were dissolved by continuous stirring in deionized water to form a solution according to the different fuel content ratio. The ratio (*Ra*) is defined as the molar ratio of total metal nitrate (MN) to citric acid (CA); *Ra*=MN:CA. They were prepared with three different Ra (1:1, 1:2 and 1:3). 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 80–90 °C under vigorous stirring until a gel formed, then the gel was dried in the oven as the dried-gel. The dried-gel was ground and calcined at the different temperature (500 °C–800 °C) for 2 h. Additionally, the residue solid was washed thoroughly with 1 mol/l HNO_3 solution and deionized water to remove the impurity (such as $SrCO_3$) and finally dried in air at 100 °C.

X-ray diffraction (Philip X'Pert model) was obtained to identify the phase present, percentage of perovskite phase and their crystallite size, in a 2θ range from 10° to 60°. And the relative amount of perovskite and impurity phase was determined by following an equation

$$\text{perovskite phase(wt\%)} = \left(\frac{I_p}{I_p + I_{im}}\right) \times 100 \quad (1)$$

The crystallite size of the calcined powders was obtained by X-ray line broadening method that estimated according to the Scherrer's formula:

$$D_{XRD} = \frac{k\lambda}{\beta\cos\theta} \quad (2)$$

The microstructure and morphology of the calcined powders were characterized by scanning electron microscopy (JOEL Leo1455VP model) and transmission electron microscopy (Philip TECNAI 12 model).

3. Results and discussion

The XRD patterns of $SrTiO_3$ powder after calcinations prepared with different Ra ratio were illustrated in Fig. 1. They showed that the perovskite phase was demonstrated, however, a mixture phases (as $Sr(NO_3)_2$ and $SrCO_3$) were found. It found that *Ra*=1:3 was predominantly found in the high intensities. Therefore, the % perovskite phase was investigated following Eq. (1) and given in Table 1.

The *Ra*=1:3 condition had the highest % perovskite phase for all calcined temperatures. Thus, this condition was coupled with an acid treatment process to remove the $SrCO_3$ impurity phase that occurred in the synthesis process.

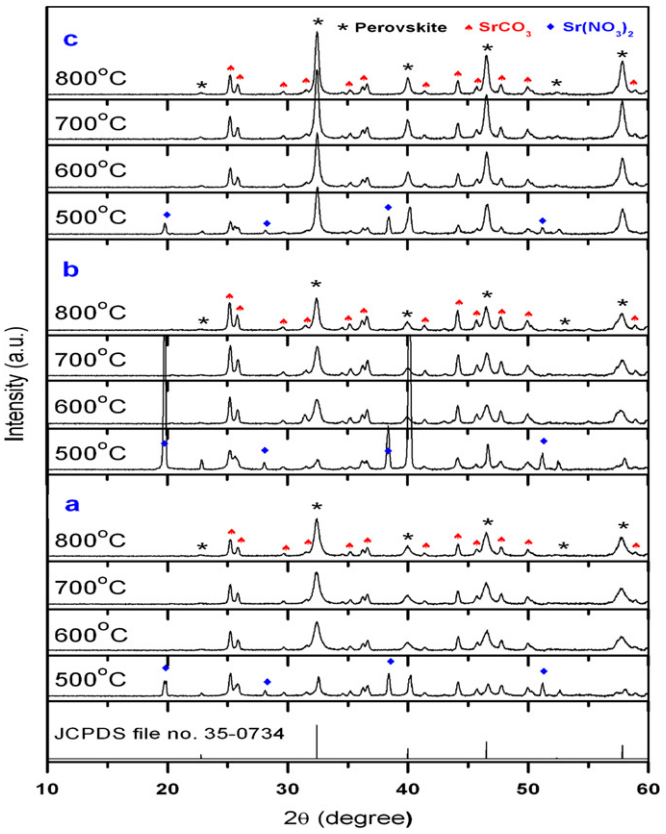

Fig. 1. XRD patterns of $SrTiO_3$ powders prepared with *Ra* of 1:1(a), 1:2(b) and 1:3(c) after calcination at various temperature for 2 h (*$SrTiO_3$).

Table 1
% perovskite phase of $SrTiO_3$ samples with different Ra ratio and calcination temperatures.

Calcination Temperature (°C)	% Perovskite phase		
	Ra=1:1	*Ra*=1:2	*Ra*=1:3
500	–	–	74.0
600	60.3	47.4	74.1
700	64.0	50.1	75.5
800	70.4	54.2	76.6

Ra=MN:CA molar ratio.

After applying an acid treatment process, the XRD pattern demonstrated that phase-pure $SrTiO_3$ was prominently illustrated as showed in Fig. 2.

They can be indexed to the cubic perovskite $SrTiO_3$ structure, correlated to $SrTiO_3$ as JCPDS file number 35-0734, lattice parameters; a=3.9050 Å, all of % perovskite phase was calculated that at a hundred percents of all cases as illustrated in Table 2.

The average crystallite sizes obtained in this condition are in the nanometers at about 23 nm. It may due to the reaction is appropriated, so that the seeds can be grown in early state and some adsorption of amorphous material around them [18]. The average crystallite size of samples

synthesized at various temperatures was calculated with Eq. (2) as showed in Table 2.

The morphology of $SrTiO_3$ samples with $Ra=1:3$ at various calcination temperatures was shown in the SEM micrograph as illustrated in Fig. 3. It is seen that almost all of the particles at various calcined temperatures were agglomerated and basically spherical in shape. The nanocrystalline $SrTiO_3$ powder exhibited a hard agglomeration. It may have occurred due to nanocrystals generally possessing large surface area and high surface energy, and have the tendency to aggregate into larger agglomeration to reduce their surface energy [19]. The average particle size of $SrTiO_3$ samples estimated from SEM micrographs to be ~50.6 nm. They are bigger than the average particle size computed by XRD data (Fig. 4).

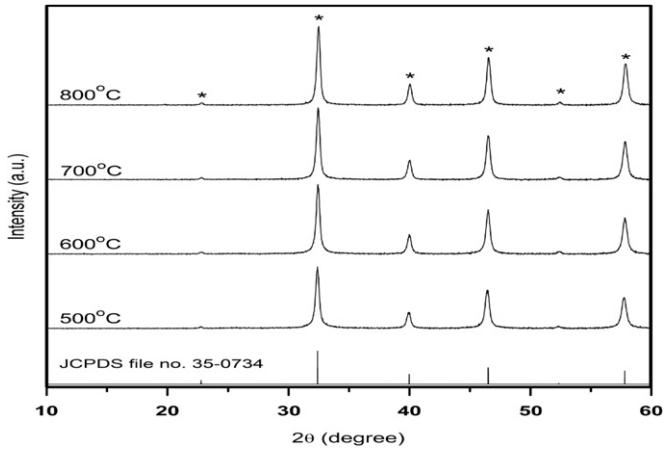

Fig. 2. XRD patterns of $SrTiO_3$ powders prepared with *Ra* ratio of 1:3 after coupled with an acid treatment process calcined at different temperature (*$SrTiO_3$).

Table 2
The crystallite size, particle size, % perovskite phase and lattice parameter of $SrTiO_3$ powders after coupled with an acid treatment process, at various calcinations temperature.

Cal. Temp. (°C)	D_{XRD} (nm)	A_{SEM} (nm)	% Perov. phase	Lattice parameters (Å)
500	22	56.2	100	3.9077
600	22	55.8	100	3.9029
700	23	45.5	100	3.9014
800	25	45.2	100	3.8988

D=Crystallite size; A=Average particle size.

It is attributed the occurrence of hard agglomeration with strong inter-particle bond reflects the microstructure of agglomerated powder. But the XRD patterns is the size of an original crystalline size. The results are presented in Table 2. The particle size was decreased with the increase of calcination temperature. The average particle size of $SrTiO_3$ powder was about 45.2 nm at the calcined temperature of 800 °C.

TEM micrographs were used to verify the morphology and particle size. They were compared before and after applying an acid treatment process at calcined temperature of 600 °C. It was found that the morphology of particle likes a spherical shape and the average particle sizes are about 8.1 nm and 7.5 nm, respectively. It was manifest that the morphology of powders is still intact without any size and shape modification after applying an acid treatment process.

4. Conclusion

The nanocrystalline $SrTiO_3$ powders are synthesized by the sol–gel combustion method with the citric acid as fuel. The phase-pure cubic perovskite structure $SrTiO_3$ were exhibited in nanometer ranges (average crystallite size from XRD is about 23 nm) at 500 °C, coupled with an acid

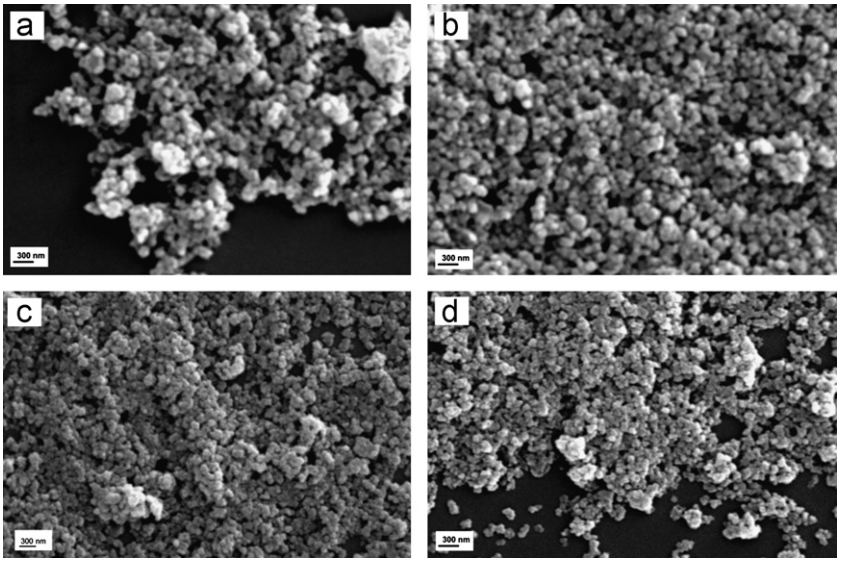

Fig. 3. SEM micrographs of $SrTiO_3$ powders prepared with *Ra* ratio of 1:3 after coupled with an acid treatment process at calcination temperature (a) 500 °C, (b) 600 °C, (c) 700 °C and (d) 800 °C, respectively.

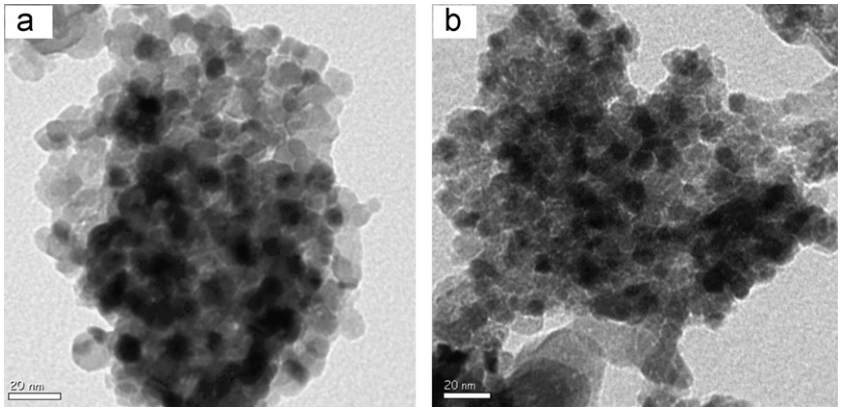

Fig. 4. TEM micrographs of $SrTiO_3$ powders prepared with *Ra* ratio of 1:3 (a) before and (b) after coupled with an acid treatment process calcined at temperature of 600 °C.

treatment process. From XRD, the crystallite size was decreased with increasing calcined temperatures. SEM and TEM observation shows that the morphology of the particles is uniform and regularly shaped like spheres. TEM average particle size was evaluated to be about 7.5 nm after coupled with an acid treatment process at calcination temperature of 600 °C.

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