

The effect of surfactant on SrTiO₃ particles synthesized by a microwave hydrothermal method

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SrTiO₃ particles with different morphologies were successfully synthesized by a microwave hydrothermal method. The effect of different surfactants on the morphology, the crystal structure and the optical property of particles were investigated. Polyvinyl alcohol-derived particles had a rodlike morphology, a large ratio of $c/a > 1$ and small band gap energy (2.60 eV). Polyethylene glycol-derived particles had a shorter rodlike morphology, smaller ratio of $c/a > 1$ and a bigger band gap energy (3.25 eV). In contrast, the carboxymethyl cellulose-derived particles had a platelike morphology, a small ratio of $c/a \sim 1$, and a broad band gap (3.34 eV). Raman analysis revealed that the either polyethylene glycol- or polyvinyl alcohol-derived SrTiO₃ particles were tetragonal, while another particle was cubic.

Key words: A: nano materials, E: optical, H: selection for material properties.

Introduction

Strontium titanate (SrTiO₃) is an ABO₃-type perovskite and can exhibit ferroelectric (FE) behavior. SrTiO₃ is a quantum paraelectric material, its FE behavior can be induced by appropriate doping, through oxygen isotope exchange, or under an applied stress. Recently, special attention has been paid to shape control of SrTiO₃ particles, which appeared to be attractive in synthesis processing and shape characterization [1-3]. In contrast to this, studies of the optical properties and microcrystalline structure of shape-controlled SrTiO₃ powders are rather limited. Perovskite materials usually show of ferroelectric behavior as their $c/a > 1$, such as, the c-oriented columnar BaTiO₃ ferroelectric films prepared by reasonable solution chemistry and thinner films [4], thinner individual layers [5, 6] and rapid heating annealing [7] possess the greater ratio of $c/a > 1$ and better ferroelectric property. In this paper, we report that the microwave hydrothermal synthesis of the powders with different surfactants, which yields SrTiO₃ powders with a rodlike and a platelike morphologies, and different lattice structures and optical properties.

Experimental Procedures

Synthesis of the SrTiO₃ particles

The starting materials used in the present study were all of analysis grade. Titanium propoxide was dissolved in ethylene glycol. The concentration of Ti⁴⁺ cation in this

solution was 0.01 M. NaOH aqueous was slowly added with constant stirring until pH~9, which caused the immediate precipitation of a white solid. An equal molar quantity of strontium hydroxide was made with the same method. The two precursors were then mixed together and stirring for 60 minutes. Polyethylene glycol (PEG), polyvinyl alcohol (PVA), and carboxymethyl cellulose (CMC) at a molar ratio of monomer : metal ions = 30 : 1 were added to the mixture of the hydroxide precursors in modified polytetrafluoroethylene resins (TFM)/ poly(ether-ether-ketone) (PEEK) autoclaves (volume : 100 ml, degree of filling : 80%V). After sealing, the mixtures were heated to 80 °C at a rate of 25 K·minute⁻¹ and then aged for 8 h. The hydrothermal reactions were carried out in an automatic frequency conversion microwave hydrothermal oven (Model No : MAS-I, China) at 200°C for 1 h. The heating rate was about 50 K·minute⁻¹. After natural cooling in the furnace, the products were washed with distilled water, then dried for 24 h at ambient temperature.

Characterization of the particles

The crystalline structure of the synthesized SrTiO₃ powders was identified at room temperature using X-Ray diffraction (XRD, CuK_{α1}, $\lambda = 0.15406$ nm, Model No : D/Max-2200PC, Rigaku, Japan). The morphology of the particles was analyzed using scanning electron microscopy (SEM, Model No : JXM-6700F, Japan). Raman spectra of the powders were analyzed using a dispersive Raman spectrometer (Model No : ALMEGA-TM, Thermo Nicolet, America). The laser beam used as the excitation source was of a wavelength of 514.5 nm and a power of 50 mW. The laser beam was focused on the sample through a 50× objective lens (numerical aperture = 0.75). The light transparency of the SrTiO₃ powder dispersed in acetylacetone solution was

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determined in the range of 300-700 nm with a UV-vis spectrophotometer (Model No: 752N, China).

Results and Discussion

Fig. 1 shows the XRD patterns of the SrTiO₃ powders synthesized by a microwave hydrothermal method. The synthesized powders all were the tausonite phase belonging to the isometric- hexoctahedral crystal system. The average particle size of the synthesized powders was calculated with Scherrer's formula (Table 1). The PVA-derived powder showed the smallest particle size, while the CMC-derived powder showed the largest size. In general, SrTiO₃ is of a cubic structure. However, special synthetic processes can cause a change from cubic to tetragonal. The lattice parameter of the powders was calculated with the relation for tetragonal structure:

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad (1)$$

If the powder is the cubic phase, then $c/a = 1$. Table 1 lists the calculated results, which indicate that PEG-, PVA- and CMC-derived powders have respectively lattice parameter ratios of $c/a > 1$, $c/a > 1$ and $c/a \sim 1$. This implies that PEG- and PVA-derived powders would be tetragonal.

The differences in the position of the peaks for the powders produced with PEG, PVA and CMC surfactants can be observed in refined XRD patterns (Fig 2). The XRD peak of the CMC-derived powder obviously shifts to a larger diffraction angle of 2θ . This implied decrease in interplanar

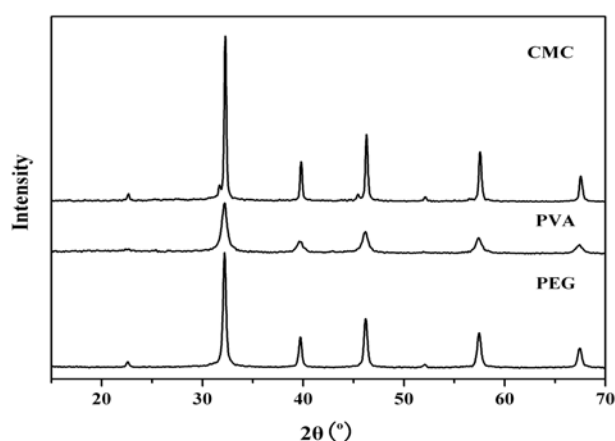


Fig. 1. XRD patterns of the powders synthesized with different surfactants.

Table. 1. Lattice parameters, particle sizes, and band gap of the SrTiO₃ powders

Suefactant	lattice parameter			particle size (nm)	band gap (eV)
	a(Å)	c(Å)	c/a		
PEG	3.9224	3.9346	1.0031	24.3	3.25
PVA	3.9232	3.9394	1.0041	15.4	2.60
CMC	3.9201	3.9157	0.9989	33.4	3.34

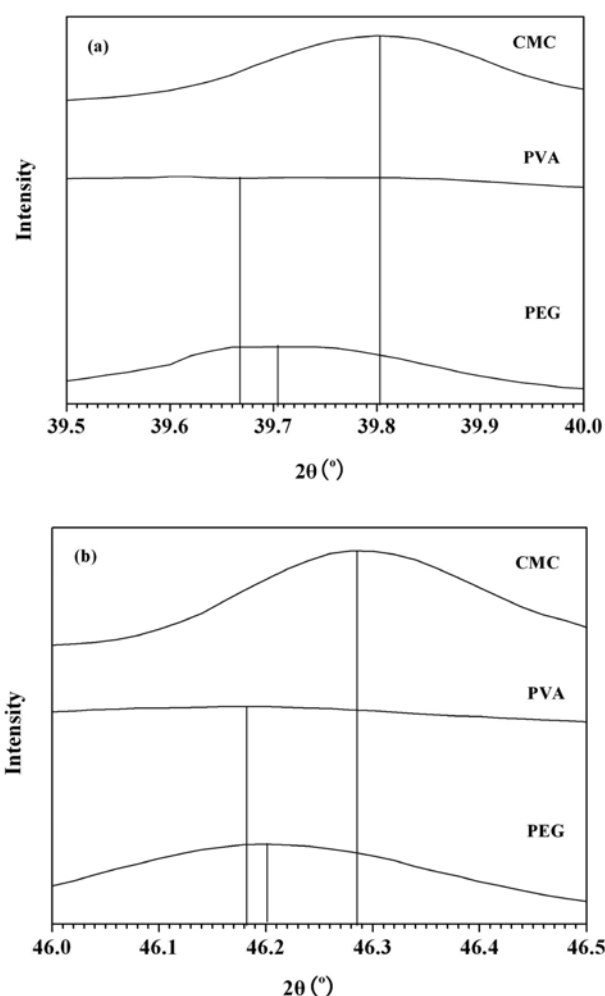


Fig. 2. Refined patterns of (a) (111) XRD peak and (b) (200) XRD peak of the powders.

spacing in Bragg's equation, agreeing to the calculated result listed in Table 1. However, this decrease in interplanar spacing is more for the (111) plane than for the (200) plane, indicating a greater decrease in the lattice parameter c . This might imply a cubic structure of CMC-derived powder.

The SEM micrographs of the SrTiO₃ powders as shown in Fig. 3 indicate that the PEG-, PVA- and CMC-derived powders were respectively of uniform short rodlike, rodlike and platelike morphologies. The average particle size of the powders increased in the order of PVA-PEG-CMC, which is consistent with the result of the XRD analysis.

The surfactant generally has many radicals that can adsorb metal hydroxides by H-bonds and some chemical interactions, and so can affect the morphology of the SrTiO₃ particles mainly by their morphology and chemical structure. PEG (CH₂OH-(CH₂CH₂O)_n-CH₂OH) has two hydroxyl radicals and certain amounts of hydrogen and oxygen that can adsorb the Sr- and Ti-hydroxides by H-bonds at the stage of aging at 80 °C. So PEG can induce the formation of chain-like hydroxides. The hydroxide chains can transfer to short rodlike crystalline in the process of following the hydrothermal reaction. The PVA (-[CH₂CH(OH)]_n-) contains

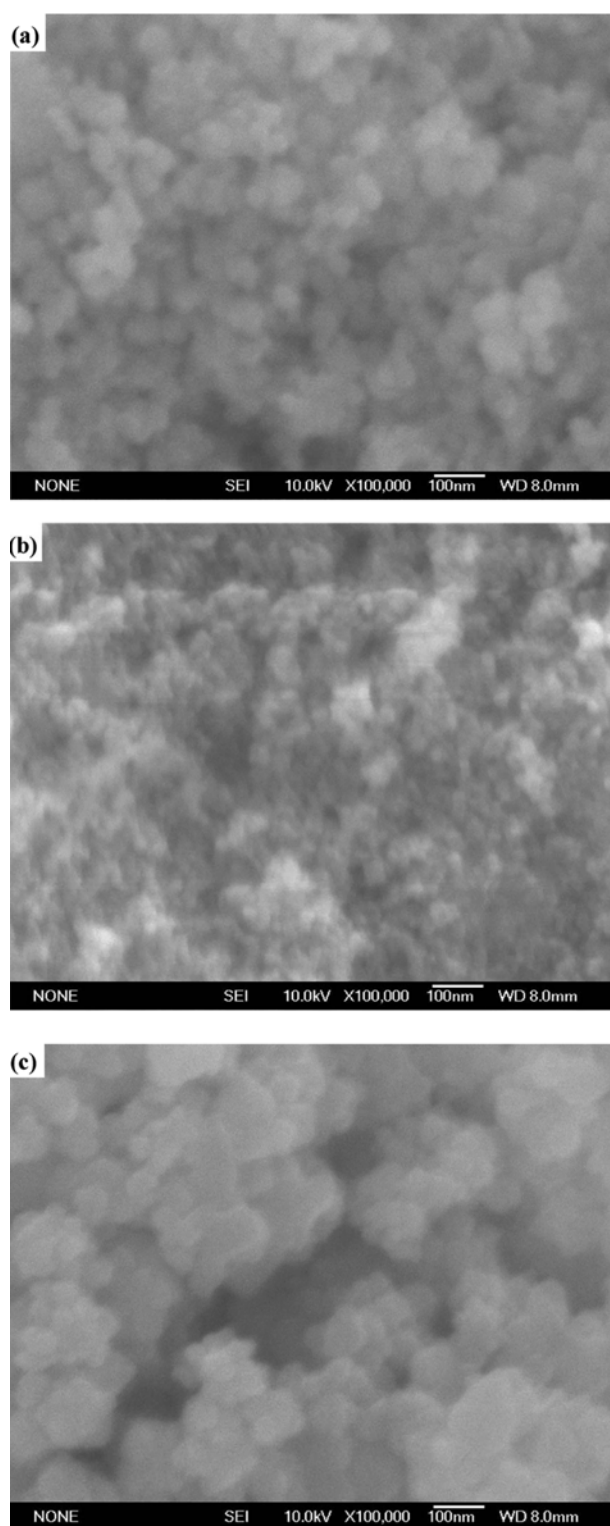


Fig. 3. SEM micrographs of the powders synthesized with surfactants (a) PEG, (b) PVA, (c) CMC.

one hydroxyl radical and two hydrogen atoms in each monomer. The molecular chain of PVA also can induce the formation of rodlike particles. By comparison, the molecular chain of PVA is more rigid, longer than that of PEG. So the PVA can induce the formation of relatively long rodlike

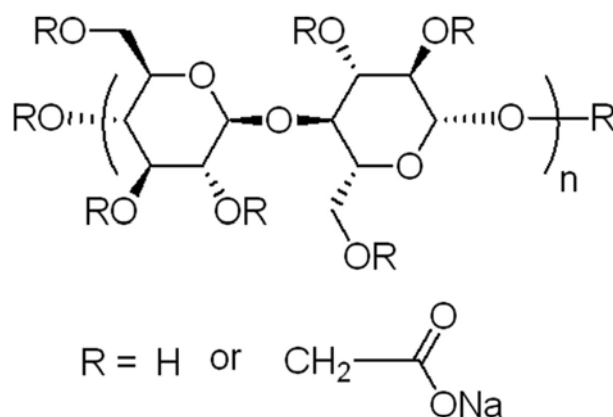


Fig. 4. Molecular structure of the carboxymethyl cellulose (CMC).

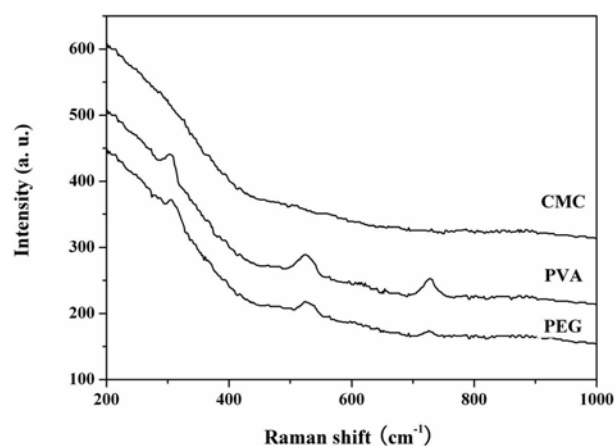


Fig. 5. Raman spectra of the SrTiO₃ powders synthesized with different surfactants.

particle. The CMC monomer contains two substituted cyclohexane tetragonal rings and some substituted radicals (Fig. 4). The substituted radical is composed of a hydroxyl radical and a sodium acetate radical on two sides of the hexagonal ring. By partially substituting the radical the CMC molecules can react with each other or with the polymer produced at an appropriate temperature. Polymerization in two-dimensions may take place. On the substituted radicals before and after the polymerization the metal hydroxides can be adsorbed by H-bonds and by substituting sodium ions by Sr and Ti ions in the hydroxides to form platelike hydroxide layers. By the microwave hydrothermal reaction, the hydroxide layers transform to the platelike SrTiO₃ particles.

In the Raman spectra of the powders shown in Fig. 5, both the PEG- or PVA-derived powders have three Raman modes at 306 cm⁻¹, 510 cm⁻¹, and 720 cm⁻¹. The 306 cm⁻¹ mode could be attributed to B₁ and E(TO + LO) modes, and the 510 cm⁻¹ mode corresponds to E(TO) and A₁(TO₃) modes. The mode at 720 cm⁻¹ could be attributed to A₁ and E(LO) modes [8-10]. These modes confirm the tetragonal structures of the PEG- and PVA-derived powders as determined by the XRD analysis. The more intense Raman peaks for the PVA-derived powder than for the PEG-derived powder indicates its more obvious tetragonal

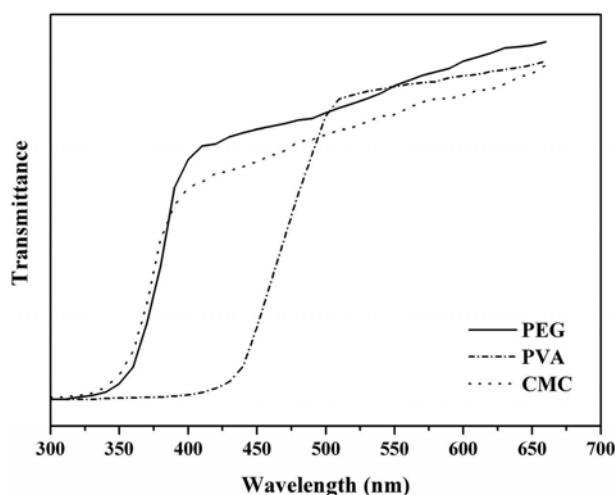


Fig. 6. Transmittance spectra of the SrTiO₃ powders synthesized with different surfactants.

structure. However, Raman spectra of CMC-derived powders do not show any mode, so the powders should be cubic.

Joshi *et al* [3], reported the synthesis of barium titanate nanowires with a surfactant-free hydrothermal method. By synchrotron XRD and Raman analyses, they believed this nanowire similarly is of tetragonal structure with $c/a = 1.0076$.

Fig. 6 shows transmittance curves of the powders, indicating transparent in the UV-visible range. A red-shift appears in the PVA-derived powder, while a blue-shift takes place in the CMC-derived powder. Tausonite structure SrTiO₃ has a direct band gap, the optical band gap (E_g) can be calculated with the following relationship [11]:

$$(ah\nu)^2 = C(h\nu - E_g) \quad (2)$$

where $h\nu$ is photon energy and C is α constant [12], and α is absorption coefficient, we assume:

$$\alpha = (1/d)(\ln 1/T) \quad (3)$$

where T is the transmittance and d is the width of the acetylacetone solution dispersing SrTiO₃ powder in the colorimetric cell. Fig. 7 shows the graph of $(ah\nu)^2$ vs. photon energy $h\nu$ for the SrTiO₃ powders synthesized with different surfactants. The linear dependence of $(ah\nu)^2$ on $h\nu$ at higher photon energies indicates that the SrTiO₃ powders are essentially direct-transition-type semiconductors. The straight-line portion of the curve, when extrapolated to zero, gives the optical band gap E_g . From the results of Fig. 7, E_g is in the range of 2.6-3.34 eV, that increases in the order of PVA-PEG-CMC (Table 1). The constant C was calculated with the reciprocal gradient of the linear portion in these curves (Table 1). In comparison with the band gap energy of SrTiO₃ crystals (3.2 eV), PVA- and CMC-derived particles are respectively of remarkably decreased and increased band gap energies, which can be mainly attributed to remarkable variations in their crystal structures. The band gap energy of PEG-derived particles only slightly increased

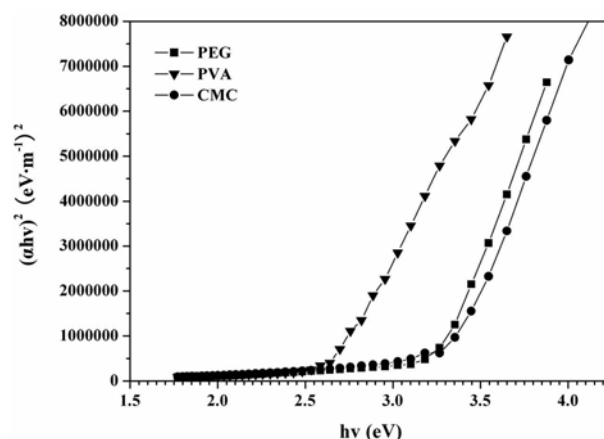


Fig. 7. Plots of $(ah\nu)^2$ vs. $h\nu$ for the SrTiO₃ powders synthesized with different surfactants.

compared with SrTiO₃ crystals. A major reason may be the well-known quantum size effect of nanoscale particles.

Tyunina *et al* [13], similarly reported that the crystal structure, orientation, and strain state of the SrTiO₃ films are all affected by single-crystal substrates. The energies of band gaps can increase due to strain-induced polarization. The absorption edge is affected by the factors of substrate surface, and thickness, strain, and polarization of film.

Conclusions

Shape-controlled SrTiO₃ powders were synthesized successfully by a microwave hydrothermal method. The particle sizes of powders are very small and are of low agglomeration. The morphology, lattice parameter, microstructure, and optical property of the powders obviously depend on the surfactant.

The PVA-derived particles have a rodlike morphologies, a larger ratio of $c/a > 1$, a small band gap energy (2.60 eV). PEG-derived particles have a shorter rodlike morphology, a smaller ratio of $c/a > 1$ and a bigger band gap energy (3.25 eV). In contrast, the CMC-derived particle has platelike morphology, a small ratio of $c/a < 1$, and the largest bandgap energy (3.34 eV). Raman analysis revealed that the PEG- and PVA-derived SrTiO₃ particles all are tetragonal, while the CMC-derived powder is cubic.

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