

Soft chemistry preparation methods and properties of strontium titanate nanoparticles

M. Makarova^{a,*}, A. Dejneka^a, J. Franc^c, J. Drahokoupil^a, L. Jastrabik^a, V. Trepakov^{a,b}

^a Institute of Physics, Na Slovance 2, 18040, Prague 8, Czech Republic

^b A.F. Ioffe Physico-Technical Institute RAS, 194 021 St-Petersburg, Russia

^c J. Heyrovsky Institute of Physical Chemistry, Dolejskova 3, 18223, Prague 8, Czech Republic

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ABSTRACT

A brief survey of chemical synthesis methods for SrTiO₃ nanoparticle fabrication is presented. The principal features of microwave, mechano-chemical, coprecipitation, sol-gel, solvothermal and template methods as well as the limits of their application are described. Special attention was paid to nominally pure and transition metals doped SrTiO₃ nanoparticles of 100–12 nm size, prepared by citrate method, their characterization, and dependence of lattice constant and optical band gap on particle size.

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1. Introduction

SrTiO₃ has a broad range of application in physics and chemistry – as highly polarizable nonlinear dielectric [1], superconducting [2], semiconducting [3], substrate [4], photocatalytic [5], solid electrolyte [6] and solid oxide fuel cells (SOFC) anode [7] material. It has been found that its properties strongly depend on the particle size in the range below 100–200 nm [8–10]. For example in [8,9] it was shown that photoluminescence (PL) intensity of SrTiO₃ nanoparticles at room temperature increases with decreasing particle size. At the same time PL pronounced in single crystals is observable at low temperatures only [11,12]. In [10] an increase of the band gap E_g and lattice constant with decreasing nanoparticle size was stated and ascribed to the presence of surface dipoles. This makes the particle size to be an important parameter for modification of properties and for design of materials with desirable characteristics.

Generally SrTiO₃ nanoparticles could be prepared by physical (magnetron sputtering, laser ablation etc.) and chemical methods. In this paper we would like to present a short survey of the most topical chemical preparation methods, discuss their advantages and main failures and compare some of the reported results with those of our own. In contrast to BaTiO₃ only few works have been reported about SrTiO₃ nanoparticle synthesis despite the chemical properties of Ba and Sr are quite close

and often the routes of BaTiO₃ preparation may be applied to SrTiO₃. Similar approach concerns PbTiO₃ and partly zirconates. However, it appears that in the solutions at the same conditions SrTiO₃ nanoparticles grow larger in size than those of BaTiO₃ (36 and 18 nm in [13], 5–10 and 4–5 nm in [14], respectively). This can be connected to the fact that growth of BaTiO₃ crystals is more hindered than that of SrTiO₃ because of the stronger binding force and capping effect of solvent molecules to BaTiO₃ than to SrTiO₃. This checks the growth rate of BaTiO₃ compared with that of SrTiO₃ [13].

It should be noticed that brief descriptions of nanosized (Ba,Sr)TiO₃ preparation methods presented in [15,16] do not mention the resulting particle sizes. A detailed review of liquid phase syntheses is given in [17], but it concerns all types of inorganic nanoparticles.

2. Results and discussion

2.1. Solid state methods

Conventional method of the SrTiO₃ phase preparation includes the solid state reaction at high temperatures ($t \approx 950$ – 1300 °C). This results in formation of coarse SrTiO₃ particles of the size 5 μm and higher [18]. Microwave heating can be used instead of thermal one too; however, it requires special precursors, like TiO(OH)₂ and Ba(NO₃)₂ in [19]. Particle size for this way is reported

* Corresponding author. Tel.: +420 266052131; fax: +420 286890527.

E-mail address: makarova@fzu.cz (M. Makarova).

to be 380 nm (measured synthesis temperatures were 600 °C and higher) which is rather large.

At the same time solid state reaction can proceed even at room temperature in case of external activation, yielding small-size particles. SrTiO₃ may be obtained mechano-chemically by 90 h milling of SrO and TiO₂. Fabrication of SrTiO₃ particles of 7 nm in size has been reported in [20]. However, the preparation in the mills may be accompanied by the pollution due to grinder material.

2.2. Wet chemistry methods

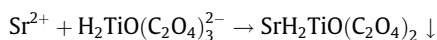
Using a liquid phase in the processing we increase the reaction system homogeneity which facilitates the phase formation. There most often used ways are sol–gel, coprecipitation, alkaline solution and solvothermal techniques. These methods can be accompanied by ultrasound, microwave radiation and nanoreactors usage. The particle size depends on reaction conditions.

A group of instrumental methods (see below) adjoins the mentioned ones. Strontium and barium titanates nanoparticles are obtained by freeze-drying [15,21], spray pyrolysis [22,23] and supercritical drying [24,25]. However, these methods have not received a wide application since special instrumentation is needed without providing results that cannot be achieved by simpler ways.

Molten salts synthesis (MSS) should be also noticed. The reaction takes place in the melt of Na and K hydroxides [26], nitrates [27] or chlorides [28,29] at temperatures 300 °C and higher, depending on the matrix. However, the product is often polluted [27] and the particles are of rather large size (50 nm [28] and higher). Therefore, so it is not widely used, except for the preparation of plate-like SrTiO₃ from Sr₃Ti₂O₇ [29].

2.2.1. Coprecipitation

This method uses well-known reaction of the insoluble strontium titanoxalate formation with its washing and further thermolysis to SrTiO₃ at temperatures higher than 500 °C:



Particle size depends on precipitation and calcination conditions. High concentrations of ions in initial solutions provide intensive nucleation and small size of particles in the product. For SrTiO(C₂O₄)₂ annealed at 550 °C the size of SrTiO₃ particles is reported to be 400 nm [16]. In our experiments the particle size of SrTiO₃ was ≈15 nm, when the precursor is annealed under vacuum at 550 °C. Another method is the coprecipitation of peroxides and the reported particle size is 50–200 nm [30].

However, the preparation of doped materials, if the additive is not Ca, Ba or Pb, may be hampered, because the demanded concentrations of doping cation might be too low and only Sr and Ti compounds would precipitate. In this regard, the work of Pfaff reporting on Mn and La precipitation at 0.006 and 0.1 mol.% level respectively under the (Ba,Sr)TiO₃ synthetic conditions should be mentioned here [30].

2.2.2. Sol–gel method

Sol–gel technique is based on the formation of colloidal sol with its further transformation to gel. The process takes place at low temperature and allows obtaining not only fine particles but also metastable phases. The method is highly effective for entering and uniform distribution of doping additives at synthesis stage [31] and has several variants, the most used being alkoxide and citrate ones.

Alkoxide methods are based on the preparation of cation solutions in waterless organic media such as alcohol, ether [9,32], tetra-

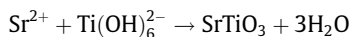
hydrofuran [33], acetic acid [34] and others. After mixing, the solution undergoes hydrolysis (or solvent evaporation [35]) to form a gel, which may be later annealed at $t \geq 500$ °C to form crystalline titanate. Such procedure allows us to obtain SrTiO₃ particles of 12 nm and higher [9]. Using reversed micelles as templates, it is possible to obtain BaTiO₃ particles of 4–6 nm in diameter by sol–gel route [32]. Sonification can facilitate the formation of titanate directly from sol phase resulting in 6–30 nm particles [36] or provide the formation of nanorods [37]. Alkoxide method is sensitive to air moisture, so it often requires a dry box.

Citrate method was first proposed by Pechini in 1967 [38]. It is based on the possibility of citric acid (CA) to form chelate complexes with cations and to join esterification reactions with polyatomic alcohols such as ethyleneglycol (EG). Reaction starts at a temperature slightly higher than 100 °C and ends at 200 °C by the formation of polymeric gel with uniformly distributed cations [31].

The optimal CA concentration is considered to be between 50 and 60 mol.%, where viscosity is the highest and smooth mild burning is provided during pyrolysis, resulting in a lower internal temperature and, consequently, particle size [39]. A stable complex (Ba,Sr)Ti(CA)₃ is formed in the system [40], so (Ba,Sr)TiO₃ nanoparticles may be obtained by combustion of citrate gel even without an addition of EG. EG acts there as a dispersant preventing the formation of hard agglomerates. Its presence in reaction mixture decreases the titanate particle size from 100 to 40 nm [41].

2.2.3. Alkaline solution and solvothermal method

These processes take place in alkaline solution according the reaction:



A mineralizer-NaOH or KOH – is used to reach the required pH. In low temperature aqueous synthesis (LTAS) the reaction proceeds at ambient pressure in strongly alkaline water solution, with fresh TiO₂·xH₂O gel and soluble Sr salt as precursors. The obtained particles are of 4–5 nm in size and have a strong tendency to aggregation [42]. Very close to LTAS is LTDS-low temperature direct synthesis [43], but it relates more to BaTiO₃ than to SrTiO₃ because of lower solubility of Sr(OH)₂. Under some conditions, the mineralizer may cause pollution, especially taking into account the proximity of ionic radii of Sr²⁺ and Na⁺. The composition of SrZrO₃ prepared by LTAS was found to be Sr_{0.72}Na_{0.28}Zr_{0.79}O_{1.9}(OH)_{1.1} [44]. However the syntheses of Na-free titanates were also reported [42]. The same feature concerns the solvothermal method.

In solvothermal method the reaction mixture is kept at increased temperature (≈200 °C) in the autoclave. Microwave heating can be also used [45]. Usually a mineralizer is necessary, but Niederberger et al. [14] reported on 5–10 nm SrTiO₃ and 4–5 nm-BaTiO₃ particles formed in the solution in waterless benzyl alcohol without any alkali.

Water [4,45,46] or organic compound [13] may be taken as a solvent. Its effect on particle growth may be illustrated in the example of Li–Ti–O spinel, where the obtained particle size constantly decreases with the increasing solvent dielectric constant, i.e. there is an enhancement of the dissolving ability. However, water is an exclusion from the row [47], so the dielectric constant is not a determinant parameter. Solvothermally prepared (Ba,Sr)-TiO₃ particles usually have the size of several tens of nanometers and more. They are larger for hydrothermal synthesis than for organic solvent one, approaching submicron and micron size [4,45]. For example, SrTiO₃ particles prepared in etanolamine–ethylenediamine mixture have 36 nm in size [13].

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