Size Effect on the Structure and Optical Properties in Nanocrystalline SrTiO$_3$

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SrTiO$_3$ nanoparticles can be prospective materials for different physical, chemical and technical applications as dielectric components, materials for catalysis and optics. Particle control may lead to new effects especially when the size becomes comparable with the fundamental dimensional characteristics such as domain size, exciton or electron length, i.e. at the level of nanomaterials. The powders of titanate with perovskite structure and particle size of 5-60 nm were obtained by solvothermal or citrate sol gel methods. The tendency to the lattice constant decrease and increase [1]. Besides, mathematically Laplace pressure is considered at conserving volume of nanoparticles and does not lead directly to lattice constant decrease. For oxides, e.g. Ce$_2$O$_3$, lattice constant increases with decreasing particle size. So does BaTiO$_3$, where it is related to the change in Ti-O bonding character [4]. For SrTiO$_3$ the lattice expansion with size decrease in the range of 12-80 nm has been reported in [5, 6] and was connected to negative pressure caused by surface-defect dipole repulsion. Strong increase of the band gap magnitude $E_g$ in SrTiO$_3$ nanoparticles has been also observed in [5]. However, in Ref. [7] we showed that in spite of such effect existed indeed, the proper intrinsic effect was more weak, and more strong $E_g$ shift was rather connected to the presence of OH groups.

Quantum paraelectric SrTiO$_3$ is one of the most popular and widely investigated model compounds of the family of highly polarizable ABO$_3$ perovskite-like oxides. At $T \approx 105$ K it undergoes an O$_1^-$–D$_{4h}^{18}$ antiferrodistortive structural phase transition. The dielectric permittivity strongly rises on cooling with an extrapolated Curie-Weiss temperature $T_C \approx 35$ K. However, at the lowest temperatures the dielectric permittivity saturates and the trend to ferroelectric ordering is suppressed due to quantum mechanical effects. However even weak perturbations and impurity admixing can induce a phase transition associated with considerable changes of physical properties. In such a case, it would be reasonable to suspect that the change of lattice constant in small enough nanoparticles can affect SrTiO$_3$ stability in respect to phase transition and ferroelectricity, too. In spite of this idea, there is still an unresolved inquisitive question whether a reduction of the particle size can lead, in some materials, to an increase in the phase transition temperature and enhancement of ferroelectric properties instead of the decrease in phase transition temperature and polar state suppression.

Relatively recently we reported R-zero-phonon ($^2E_g \rightarrow ^4A_{2g}$) line luminescence as spectroscopic probe of Cr-doped SrTiO$_3$ nanoparticles [8]. It was shown that 100-200 nm nanoparticles revealed temperature behavior characteristic for incipient ferroelectrics, when energy of R-line decreased at cooling. Surprisingly in particles with size less than 20 nm, R-line revealed a minimum of energy at $\approx 19$ K for 13 nm particles that have been treated as a hint of polar phase formation. So technology development for smallest nanoparticles fabrication and study of size effect on the properties of SrTiO$_3$ nanoparticles seem, in this context, actual and attractive.

If the metal or simple oxide particles can be easily obtained in ultrafine range, complex oxides such as SrTiO$_3$ are usually studied starting from 10-15 nm [5–
SrTiO$_3$:Cr nanoparticles were obtained using two-phase solvothermal method based on one described in Ref. [11]. Strontium acetate hemihydrate was at 300°C dissolved in oleic acid in a molar ratio of 1:6. 0.7 mmol of titanium n-butoxide was mixed with 0.8 mmol of strontium oleate solution and 11 ml of toluene. Sr was taken in excess to take into account the possible SrCO$_3$ formation (due to adsorption of air CO$_2$ by the precursors) and prevent the formation of TiO$_2$ in the product. Then 3.5 ml of the 4M NaOH solution with a small addition of Cr(NO$_3$)$_3$·9H$_2$O as 0.01 mol.% towards Ti was added. The mixture was placed into 20 ml Teflon cup, which was sealed into a stainless steel autoclave, placed into an oven preheated till 180°C and kept for 12 hours at this temperature. To obtain bigger quantities, the synthesis was repeated several times with every new portion. After the synthesis, the upper transparent toluene phase was separated from the lower water one and mixed with 3-4 volumes of ethanol. White yellowish precipitate was collected and re-dispersed in toluene. Then again the 3-4 volumes of ethanol were added and precipitate was collected and dried. To remove the excess of Sr, the powder was washed with 1M acetic acid. To obtain a set of powders with different particle size the obtained samples were annealed in air for 1 hour at 400, 600 and 800°C respectively.

Powders were studied with XRD at PANanalytical X’pert diffractometer with CoKα radiation and Ag powder taken as an internal standart. UV-Vis reflectance spectra were recorded at room temperature using the Perkin-Elmer Lambda 19 UV-Vis-NIR spectrophotometer equipped with an integrating sphere. BaSO$_4$ plate was used as a reference standard. The measured spectra were transformed into absorbance according to the Schuster-Kubelka-Munk theory. Absorption edge value was determined as onset point. 5 μm SrTiO$_3$ powder (Aldrich, 99%) was taken as a bulk material. Transmission Electron Microscopy (TEM) was performed at JEOL JEM-1200 EX with CCD camera Mega View III from Soft Imaging System. Accelerating voltage was 120 kV. Atomic force microscopy (AFM) measurements were performed at Molecular Imaging Picoscan 2500 with PicoSPM II controller. Raman spectra measurements were performed at room temperature with Renishaw InVia Raman Microscope facility with experimental sample was illumination by 488 nm of blue laser beam (“Stellar-REN” of Modu-Laser llc) and spectra collected by 100x Leica objective.

II. EXPERIMENTAL

FIG. 1. XRD pattern of obtained SrTiO$_3$ samples compared to the pattern of standart SrTiO$_3$, rutile and anatase.

FIG. 2. Dependence of lattice constant on coherent domain size in nanosrystalline SrTiO$_3$ powders. Powders with size below 10 nm were prepared with solvothermal method as described in Experimental part. Coarser particles were prepared with Pechini-like method in Ref. [7].

FIG. 3. TEM image of SrTiO$_3$ prepared with solvothermal method (as-prepared).
III. RESULTS AND DISCUSSIONS

In Fig. 1, we can see that the as-prepared powder is a single phase SrTiO₃ with only additional peak at 2θ = 24.3 and 48.7. Since these peaks do not present in annealed powders, we assume that they come from organic shell around the particles. Sample, annealed at 400°C is also a single phase SrTiO₃, but in the powder annealed at 600°C a small amount of anatase phase appears. Annealing at 800°C leads to emergence of both rutile and anatase admixture peaks, which content corresponds to 26 and 6 vol.%, or 46 and 11 mol.%. These peaks are much narrower than in SrTiO₃, which remains broad even after high temperature annealing. This shows that SrTiO₃ particles remain fine while TiO₂ phases grow to tens of nanometers.

Lattice constant of the initial sample and samples annealed at 400, 600 and 800°C was found to be 3.913, 3.912, 3.911 and 3.908 Å, respectively (3.905 Å in bulk crystals [8]). Coherent domain size changed from 5-6 nm in as-prepared sample and the samples annealed at 400 and 600°C to 7-8 nm for the one annealed at 800°C (Fig. 2). TEM shows that as-prepared sample has particle size of 5 nm (Fig. 3), so does AFM (Fig. 4), which means that particles are single-domain without inner blocks. However, the particles have a tendency to aggregate into 2D structures of 100-200 nm size (Figs. 3 and 4). As the lattice constant shows clear tendency to increase with particle and coherent domain size decrease, that can be tentatively connected to negative pressure effect [5, 6], which becomes much stronger for particle size less than 10 nm (Fig. 2).

In Fig. 5, we can see UV-Vis spectra, where as-prepared sample has pronounced Urbach’s tail, which, however, gets depressed after annealing at 400 and 600°C. This may be connected as with the decrease of defect amount and adsorbed surface groups as with the burning of organic shell. A strong rise of absorbance takes place in the region of 3.22 eV that is less than that 3.3 eV for indirect gap in the bulk and it evidences that decrease of band gap value in very small particles is caused by presence of titanium oxide phase, Sr depleted layers or organic shell. The higher absorbance values for nanopowders compared to the bulk could be connected to the lower size, higher...
The fact that XRD peaks of SrTiO$_3$ composite or core-shell particles. As we noticed earlier, after annealing at 800$^\circ$C and powders annealed at lower temperatures. But sorption edge itself does not change which correlates with ones. Other spectra are of the as-prepared SrTiO$_3$ (gray), annealed at 400 (blue), 600(green) and 800$^\circ$C (red). Assignment is taken from Ref. [12] for TiO$_2$ modes and Ref. [13] for SrTiO$_3$ ones.

amount of boundaries and increased scattering. The absorption edge itself does not change which correlates with the similarity of particle sizes for the as-prepared powder and powders annealed at lower temperatures. But after annealing at 800$^\circ$C it moves from 3.22 eV in as-prepared sample to 3.07 eV in the annealed one. The later value corresponds to pure rutile absorption edge, despite the amount of rutile is estimated from XRD to be only 26 vol.%. No second absorption edge which could be assigned with SrTiO$_3$ is observed. The data on absorption edge are summarized in the Fig. 6. While quantum size effects should result in band gap increase with size decrease, we see clear maximum. That could witness that SrTiO$_3$ nanoparticles are incapsulated: as prepared sample into organic shell, annealed- into TiO$_2$ phase, forming composite or core-shell particles. As we noticed earlier, the fact that XRD peaks of SrTiO$_3$ are broader than rutile and correspond to much smaller coherent domain size, may be ascribed to the absence of direct contact between inner SrTiO$_3$ phase particles. This prevents fritting and hinders the element diffusion, while rutile phase grows freely.

Raman spectra (Fig. 7) demonstrate that in the as-prepared powder SrTiO$_3$ perovskite modes coincide with ones in the 20 nm nanopowder taken as a standard. No mode related to TiO$_2$ phases is visible. For the sample annealed at 400$^\circ$C we see the peak of anatase $E_{g}$ at 90 cm$^{-1}$ and LO$_2$+TO$_3$ modes of SrTiO$_3$. Rutile peak observation is suppressed by strong luminescence at higher values of Raman shift. For the sample annealed at 600$^\circ$C we do not observe a strong peak of $E_{g}^{\text{at}}$, and the peak at 620 cm$^{-1}$ can be still ascribed to anatase [12], so we do not see rutile phase. This observation is supported with XRD data. After annealing at 800$^\circ$C rutile phase modes $E_{g}$ and $A_{1g}$ appear, but anatase peaks are still present. No SrTiO$_3$ modes are seen in the spectra of samples annealed at higher temperatures. This could also confirm the suggestion of SrTiO$_3$ inside TiO$_2$. However, despite inversion center presence, anatase symmetry supposes also first order Raman scattering, while SrTiO$_3$ spectrum should contain only second order peaks with low intensity, and the spectra could be explained by invisibility of SrTiO$_3$ in the presence of TiO$_2$.

We can suppose that the surface layer of as-prepared SrTiO$_3$ is Sr-depleted and Ti-rich, despite no TiO$_2$ phase is found there. That could be the consequence of acetic acid washing, but, however, it could be the intrinsic property too. It was determined that the compounds and composition, not stable in the bulk, may be stabilized in nanostate due to increasing role of surface defects [14–16]. In the present case the chemical formula could be written as Sr$_{0.43}$TiO$_2$H$_x$[V$_{Sr}$]$_{0.57}$[V$_{O}$]$_{1-x}$, where H belongs to structural water and hydroxyl groups, and V are the vacancies of Sr and O. During heat treatment the compound decomposes into SrTiO$_3$ and TiO$_2$ phases (Fig. 8). According to UV-Vis and Raman spectra they form core-shell structure with TiO$_2$ around SrTiO$_3$. This suggestion needs to be checked with TEM. However, it is not easy task, because oxide nanoparticles without organic shells are usually strongly aggregated and TiO$_2$ particles are coarse.
IV. CONCLUSIONS

In conclusion, we observed the increase of SrTiO$_3$ lattice constant with nanoparticle size decrease, which is most pronounced in the region below 10 nm. However, we did not see clear tendency for the absorption edge, probably due to its sensitivity to the surface states caused by sample history. Thermal treatment of the nanoparticles leads to the formation of admixture TiO$_2$ phases with the size of tens of nanometers. TiO$_2$ likely forms a shell around SrTiO$_3$ particles, which remain below 10 nm in size even after 800$^\circ$C annealing.

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