SHG of Single $BaTiO_3$ Nanoparticles down to 22 nm Diameter

Eugene Kim †, Andrea Steinbrück †, Maria Teresa Buscaglia ‡, Vincenzo Buscaglia ‡, Thomas Pertsch †, and Rachel Grange †

† Institute of Applied Physics, Abbe Center of Photonics, Friedrich Schiller University Jena, Germany

‡ Institute for Energetics and Interphases, Department of Genoa, National Research Council, Italy

ACS Nano, **2013**, *7* (6), pp 5343–5349

Zaure

2013.10.05

Abstract

- SHG from single ferroelectric $BaTiO_3$ nanoparticles
- a diameter range - 70 nm down to 22 nm
- a far-field optical microscope coupled to an infrared femtosecond laser

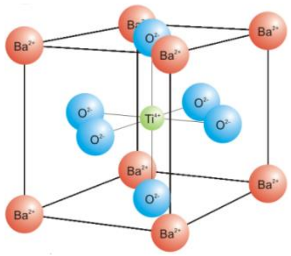
opens up the possibilities

- of using them as bright coherent biomarkers
- to investigate ferroelectricity at the nanoscale

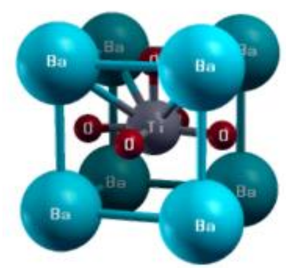
Introduction

- **Ferroelectric**
  - **Dipole moment**
  - **Ordering of dipole moments**

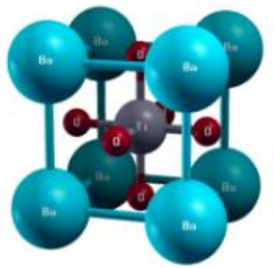
centrosymmetric



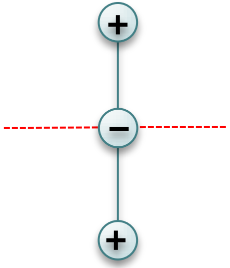
noncentrosymmetric



barium titanate crystal

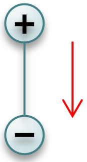


Centrosymmetric



$d = 0$

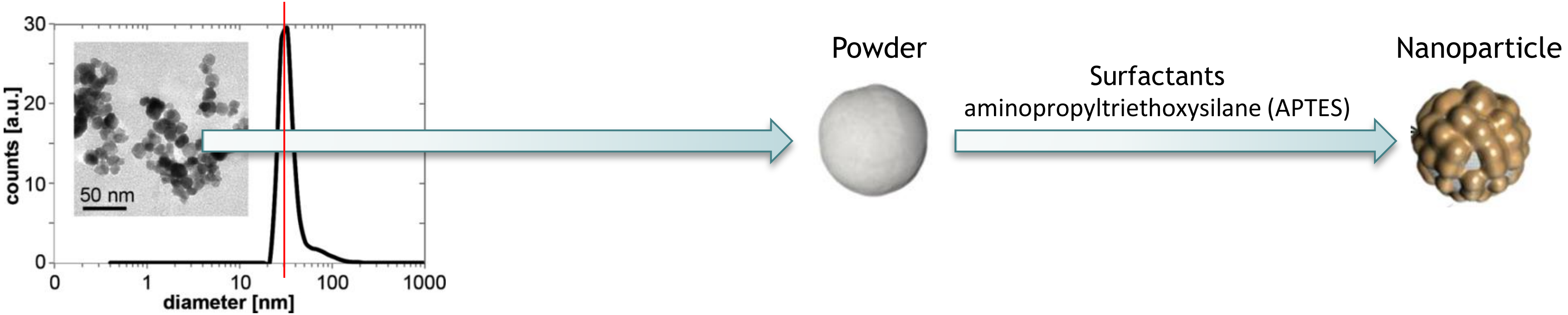
Noncentrosymmetric



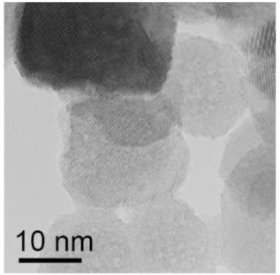
$d \neq 0$

Distortion at the surface

Particle Synthesis and Colloidal Suspension



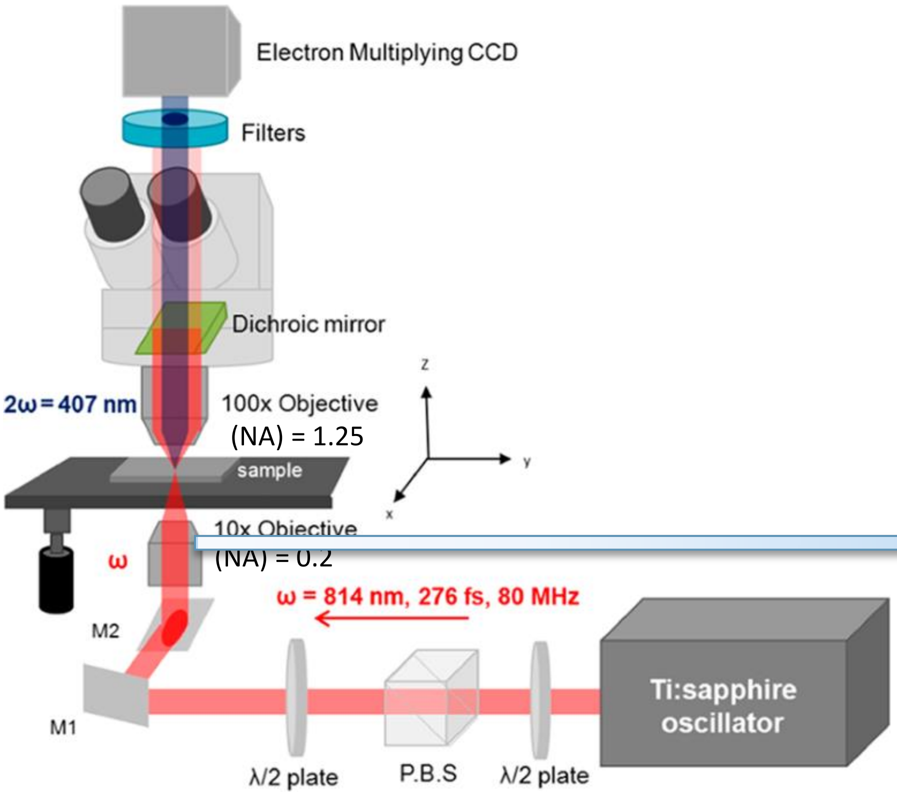
The transmission electron microscope image

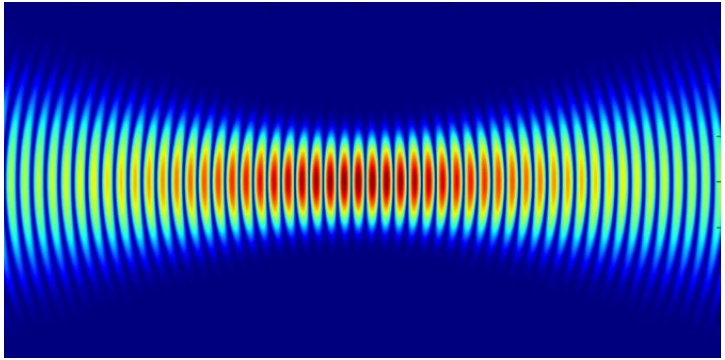


A dried powder → functionalized the surface with primary amine using APTES to obtain a stable colloidal suspension in an ethanol/water solution.

Size distribution measurement with dynamic light scattering (DLS) method gave a peak centered at 32 nm

Optical Transmission Microscope



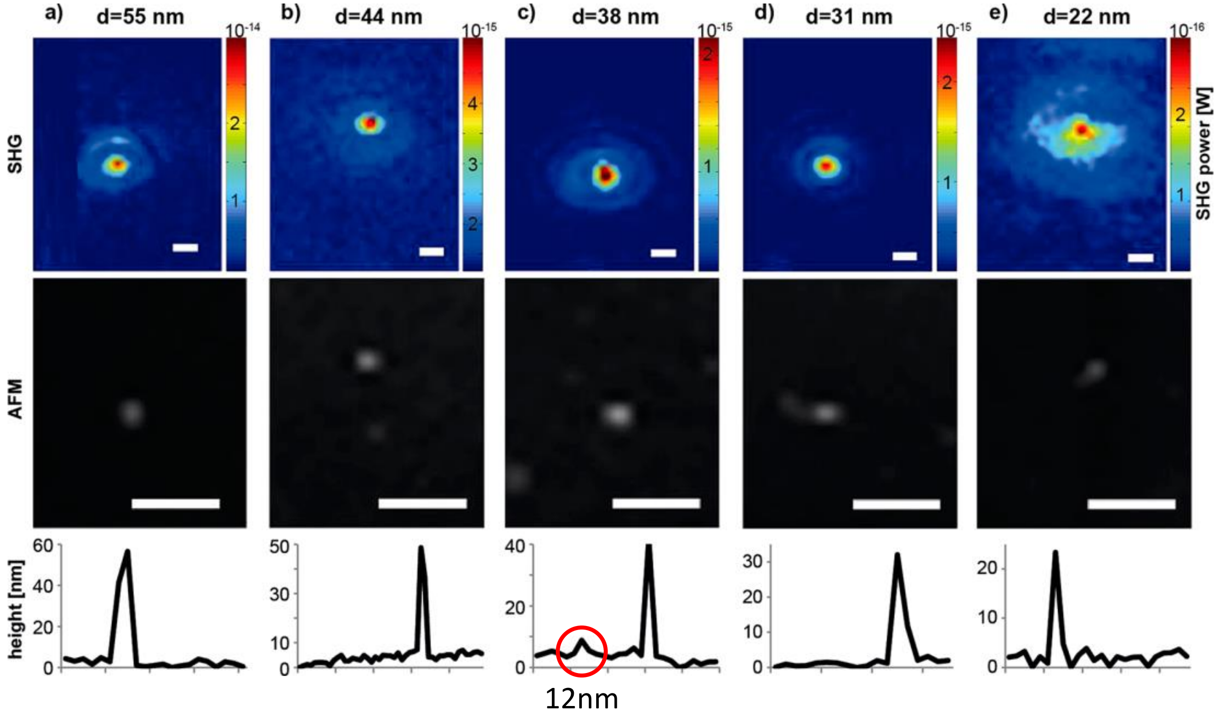


the beam is focused to 3.2 μm in diameter by an objective onto the sample plane

Measured SHG and AFM image

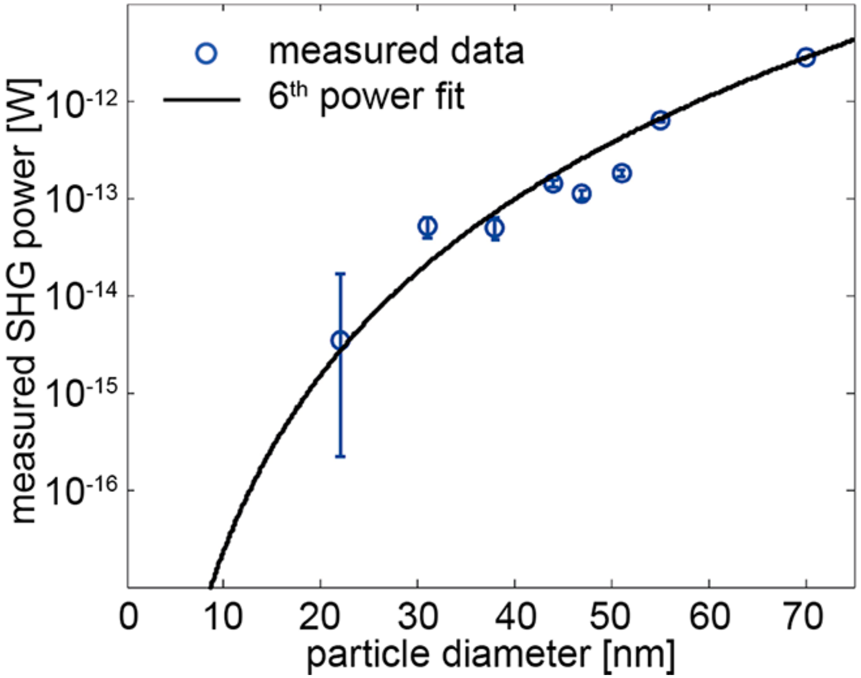
From CCD

One scan of AFM at max point



[Figure 3](#)

Relation of $BaTiO_3$ nanoparticle diameters and the logarithm of the SHG power

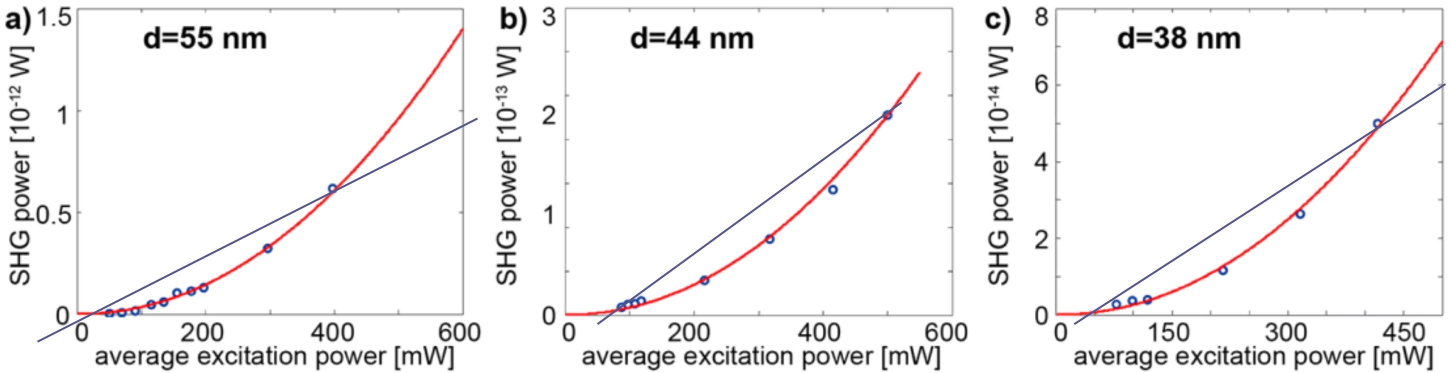


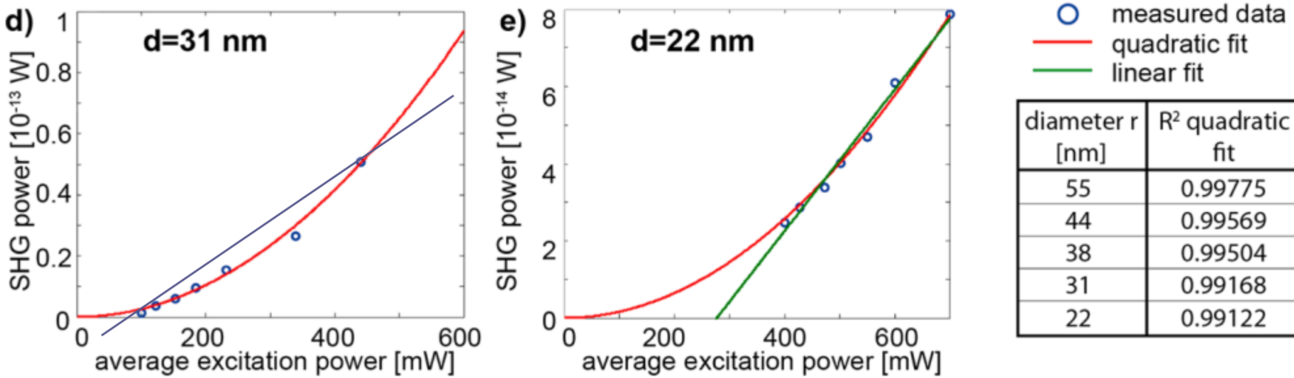
$$I \sim V^2$$

$$V \sim d^3 \quad \rightarrow \quad I \sim d^6$$

6th power law

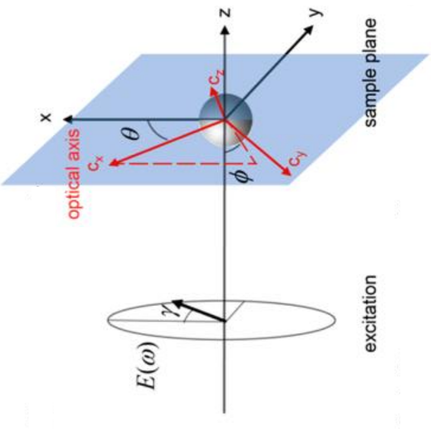
SHG power dependency

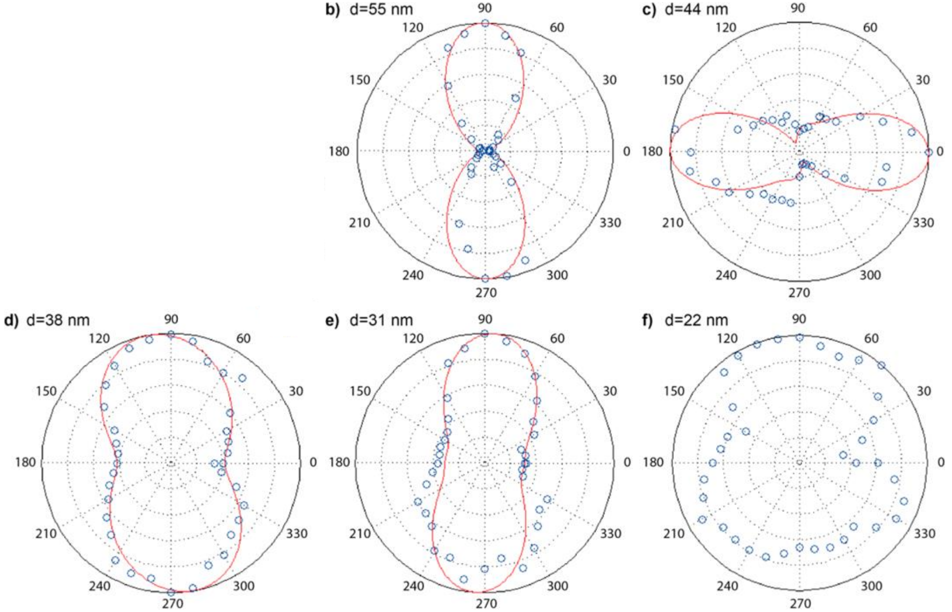




diameter r [nm]	R^2 quadratic fit	R^2 linear fit
55	0.99775	0.93883
44	0.99569	0.94920
38	0.99504	0.94027
31	0.99168	0.96324
22	0.99122	0.98772

The measurement of the polarization-dependent SHG



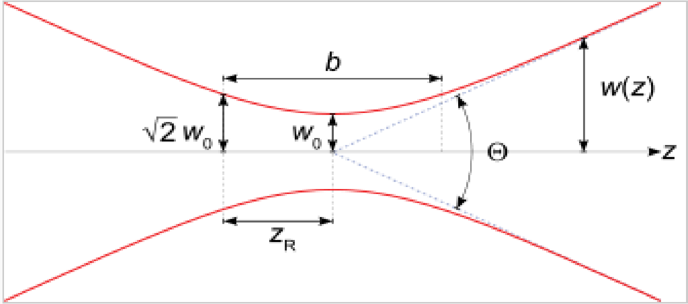


Conclusion

- The authors conclude that the 22 nm particles of noncentrosymmetric BaTiO3 is exceptional in properties judging by SHG effects and the deviations from the “normal” behavior of larger particles can be attributed to peculiar core-shell structure of the particle.
- The authors also conclude that their data on 22 nm particle indicate the presence of either tetragonal core-shell cubic structure or surface disorder in the nanoparticle.
- They are going to perform some more calculation in order to prove their conclusion.
- They claim that their method is outstanding in investigation of ferroelectricity and biomarker response in extremely small nanoparticles.

Gaussian beam

$$E(r,z) = E_0 \frac{w_0}{w(z)} \exp\left(\frac{-r^2}{w(z)^2} - ikz - ik\frac{r^2}{2R(z)} + i\zeta(z) \right)$$



Gaussian beam width $w(z)$ as a function of the axial distance z. w_0: beam waist; b: depth of focus; z_R: Rayleigh range; Θ: total angular spread

The corresponding time-averaged intensity (or irradiance) distribution is

$$I(r,z) = \frac{|E(r,z)|^2}{2\eta} = I_0 \left(\frac{w_0}{w(z)} \right)^2 \exp\left(\frac{-2r^2}{w^2(z)} \right) ,$$

where $I_0 = I(0,0)$ is the intensity at the center of the beam at its waist. The constant η is the characteristic impedance of the medium in which the beam is propagating.

For a Gaussian beam propagating in free space, the spot size (radius) $w(z)$ will be at a minimum value w_0 at one place along the beam axis, known as the *beam waist*. For a beam of wavelength λ at a distance z along the beam from the beam waist, the variation of the spot size is given by[1]

$$w(z) = w_0 \sqrt{1 + \left(\frac{z}{z_R} \right)^2} .$$

where the origin of the z-axis is defined, without loss of generality, to coincide with the beam waist, and where[1]

$$z_R = \frac{\pi w_0^2}{\lambda}$$

is called the Rayleigh range.

http://en.wikipedia.org/wiki/Gaussian_beam