Second harmonic generation in nanoparticles with Mie resonances

K S Frizyuk¹,², D A Smirnova³, A N Poddubny⁴, M I Petrov¹
1. Centre for Nanophotonics and Metamaterials, ITMO University, Saint-Petersburg, Russia
2. Academic University, Saint-Petersburg, Russia
3. Institute of Applied Physics, Russian Academy of Sciences, Nizhny Novgorod 603950, Russia
4. Ioffe Institute, St Petersburg 194021, Russia
E-mail: k.frizyuk@metalab.ifmo.ru

Abstract. We study second harmonic generation (SHG) by high-index dielectric nanoparticles and possessing bulk quadratic nonlinearity of a tensorial form. The nanoparticles exhibit Mie resonances in infrared and optical regions. We theoretically show how the polarization structure of the Mie modes governs the SHG process, and demonstrate that the superposition of two resonances at the incident light wavelength and at the SH wavelength provides us the enhancement of SHG. We also perform the multipolar decomposition of second harmonic radiation, and show that it is governed by the selection rules, defined by the symmetry of the nanoparticle shape, incident wave polarization and crystalline symmetry of the lattice.

1. Introduction
The resonantly enhanced second harmonic generation (SHG) is well studied in metallic nanoparticles [1], where the enhancement of local electric field is achieved due to strong plasmonic resonances. The plasmonic nanostructures emit nonlinear signal due to surface effects or by breaking the symmetry of the excited modes [4] as the bulk second order susceptibility tensor \( \hat{\chi}^{(2)} \) is equal to zero [2] due to inverse symmetry of the lattice. All-dielectric nanophotonics has been intensively developed over the last years as an alternative to plasmonics, with pronounced Mie-type volume resonance instead of surface plasmon resonances. The nonlinear effects accompanying the light scattering, such as second- and third-harmonic generation, are also susceptible to the resonance properties of the dielectric nanostructures. At the same time, the variety of dielectric and semiconductor materials allows one to use of those with non-zero bulk second order susceptibility tensor \( \hat{\chi}^{(2)} \). This allowed the researchers to observe strong enhancement of SHG in dielectric and semiconductor materials reported recently in number of papers [6, 9, 7, 8, 10]. However, to control the efficiency of SHG, it is vitally important to identify the mode coupling mechanism in a nonlinear process: eigen modes of a nanostructure at the fundamental frequency couple to the modes at the second harmonic (SH), with account for the specific tensor \( \hat{\chi}^{(2)} \) structure. The symmetry of both fundamental modes and SH modes, multiplied over the crystalline symmetry, either allow or forbid the typical coupling channels. This work is devoted to theoretical studies of the SHG by spherical dielectric nanoparticle. According to Mie theory, subwavelength nanoparticle with high refractive index \( n \) has first-order resonances when \( \lambda \sim nd \), where \( \lambda \) is incident light wavelength and \( d \) is nanoparticle
characteristic size. We consider the enhancement of the SHG due to Mie mode excitation, and their coupling at the fundamental frequency and at the frequency fo the second harmonic.

2. Coherent and incoherent light emission

It is well known that the emission process is defined by the local density of the optical states (LDOS) or imaginary part of Green’s function [3]. The Raman emission is dielectric nanostructures is one of the examples of such process [5]. At the same time the SH is a coherent non-elastic scattering process. One can derive the expression for the intensity of the SH emission basing on the Green’s function properties:

\[ I_{SH} = \frac{\omega_{SH}^3}{2} \left[ \int d\mathbf{V'} d\mathbf{V''} \mathbf{P'}(\mathbf{r}', \omega_{SH}, \omega) \hat{\mathbf{G}}(\mathbf{r}', \mathbf{r}'', \omega_{SH}) \mathbf{P}(\mathbf{r}, \omega_{SH}, \omega) \right], \]  

where \( \omega_{SH} \) is the second harmonic frequency, \( \mathbf{P}(\mathbf{r}, \omega_{SH}, \omega) \) is the induced polarization vector on SH double frequency. One can notice that here the intensity of SH process is defined by the cross density of states (CDOS) [11], which is defined by the imaginary part of dyadic Green function of dielectric sphere \( \hat{\mathbf{G}}(\mathbf{r}', \mathbf{r}'', \omega_{SH}) \). According to Mie theory, exciting field is significantly enhanced at specific frequencies, which gives an enhancement to non-linear response respectively. When it’s expanded into vector spherical harmonic series, coefficients before tensorial products of harmonics have resonant character. They have maximums at the same frequencies as Mie coefficients. Thus, if the \( \omega_{SH} \) is resonant, SH signal will be enhanced due to Green’s function poles even if incident light frequency \( \omega \) is out of the resonance resonant. We are interested in the cases when both wavelengths are resonant.

3. Modelling the SHG emission

We consider SH field generated by a spherical dielectric nanoparticle with sizes of the order of hundreds nanometers in diameter with high refractive index \( n \sim 2.5 - 3.5 \). Such nanoparticles have Mie resonances in the optical range. We developed rigorous analytical approach to compute and predict nonlinear fields generated by such nanoparticles and applied it to SHG from AlGaAs (Td crystalline symmetry) and BaTiO\textsubscript{3} (C\textsubscript{4v} symmetry) nanoparticles assumed monocrystalline. We used electromagnetic dyadic Green’s function approach in order to model the SH emission.

Nonlinear field at the frequency \( 2\omega = \omega_s \) outside the sphere can be expressed through the vector harmonic expansion, which give the following expression for the intensity of SHG:

\[
E(\omega_{SH}, \mathbf{r}) = \sum_{n=1}^{\infty} \sum_{m=0}^{n} E_0(D_{Menn}M_{enn}^{(1)}(\omega_{SH}, \mathbf{r}) + D_{Monn}M_{omn}^{(1)}(\omega_{SH}, \mathbf{r}) + D_{Nenn}N_{enn}^{(1)}(\omega_{SH}, \mathbf{r}) + D_{Nonn}N_{omn}^{(1)}(\omega_{SH}, \mathbf{r}))
\]

where \( M_{enn}(\omega) \) and \( N_{enn}(\omega) \) are vector spherical harmonics defined in [12].

As a basic example, we have considered BaTiO\textsubscript{3} nanosphere under non-resonant excitation, when the excitation wavelength is much longer than the lowest resonance wavelength. This provides the condition of magnetic dipolar resonance at the SH frequency. To achieve deeper understanding of the nonlinear signal properties, we decomposed the fields at the fundamental wavelength into the sum of magnetic \( M_{enn} \) and electric \( N_{enn} \) vector spherical harmonics defined in Ref. [12]. We performed the calculations and built multipolar decomposition of the SH intensity dependent from the orientation of crystalline lattice of the nanosphere (Fig. 2). We have observed the contribution of the dipolar multipoles in the total intensity on the wavelengths of magnetic dipolar resonance.
Figure 1. Geometry of the problem. We consider SHG from monocrystalline spherical nanoparticle with different lattice orientations, while incident field orientation is fixed.

Figure 2. Angular dependence of $D_{\omega mn}$ coefficients before Mie harmonics in SHG field. BT spherical monocrystalline nanoparticle, $r = 120$ nm, incident wavelength - 1200 nm. Dashed lines have been computed in COMSOL and solid lines show the analytical result.

Although intensity is expected to be enhanced due to resonance behavior of Green’s function, it can be noticed that the enhancement takes place only for particular lattice orientation. This effect is observed because the excitation of magnetic dipolar modes $M_{\omega mn}$ can be prohibited due to relative symmetry properties of the incident wave and crystalline lattice, Fig. 2 illustrates this case when $\beta = 0$.

Using symmetry properties of the system, we developed simple rules to find if particular Mie-harmonics are presented in SH-field. We provide table of the selection rules when BT lattice-axis orientation is parallel to $k$-vector of incident field ($\beta = 0$) (table 1). We consider only dipolar terms in incident field. For the first case, magnetic dipoles are not presented in SH field, and can not be enhanced by resonant LDOS on the frequency of MD resonance.

Table 1. Selection rules for BT when $\beta = 0$. The magnetic dipoles are not presented in the SH field.

| incident field | Second harmonic contains |
|----------------|-------------------------|
| $N_{e11} \times N_{e11}$ | $N_{e01}, M_{o22}, N_{e03}, N_{e23}, M_{o24}, N_{e05}, N_{e25}$ |
| $M_{o11} \times M_{o11}$ | $N_{e01}, M_{o22}, N_{e03}, N_{e23}$ |
| $M_{o11} \times N_{e11}$ | $N_{e02}, N_{e22}, M_{o23}, N_{e04}, N_{e24}$ |

As one can see from the selection rules, the total SH intensity is dependent on the relative orientation of the incident plane wave and the crystalline lattice.

The same rules can be applied for the other crystalline symmetries such as AlGaAs with $T_d$ lattice group. We build the multipolar decomposition of the intensity dependence on nanoparticle radius for SHG by a spherical AlGaAs nanoparticle (Fig. 3). We see that the SH signal is enhanced when we have resonances at incident and SH wavelengths, but modulated by selection rules (not all spherical harmonics appear). In particular, all electric dipolar harmonics are prohibited for $T_d$ symmetry when the incident field is parallel to crystalline lattice axis.
Fig. 3. Multipolar decomposition of SHG intensity in AlGaAs nanoparticles of different radius. Pump wavelength - 1550nm.

4. Conclusion
We have analyzed the second harmonic generation from crystalline noncentrosymmetric nanoparticles, possessing second-order bulk nonlinearity. We derived the selection rules for typical crystalline systems and validated them with numerical modeling. We have calculated the dependence of the SH intensity on the orientation of the crystalline axes with respect to the incident light polarization. The maximum conversion efficiency was found to be achieved when both incident and SH wavelength are resonant, and resonant multipoles are not prohibited by the selection rules.

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