Magic high-order harmonics from a quasi-one-dimensional hexagonal solid

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Abstract

High-order harmonic generation (HHG) from atoms is a coherent light source that opens up attosecond physics, but it is the application of HHG to solids that brings much of excitement for the last decade. Here we report a completely new kind of harmonics in a quasi-one-dimensional and hexagonal barium titanium sulfide: Under circularly polarized laser excitation, harmonics are generated only at first, fifth, seventh and eleventh orders. These magic harmonics appear only with circularly polarized light, not with linearly polarized light. Neither cubic nor tetragonal cells have magic harmonics even with circularly polarized light. Through a careful group-theory analysis, we find that two subgroups of symmetry operations unique to the hexagonal symmetry cancel out third and ninth harmonics. This feature presents a rare opportunity to develop HHG into a crystal-structure characterization tool for phase transitions between hexagonal and nonhexagonal structures.
I. INTRODUCTION

High-order harmonic generation (HHG) from solids [1] and nanostructures [2–5] has been extended to a broad scope of materials (see references in [6–8]). With strong signals and large tunability of energy spectra, solid-state HHG has reshaped the landscape of HHG as a radiation source from simple atoms, and has gradually developed into a practical tool to characterize materials properties on unprecedented short time scales, where the motion of electrons can be pictured frame by frame within several hundred attoseconds. Naturally, not all the processes such as chemical reactions require such short time scales, but many do. For instance, to resolve laser-induced ultrafast spin dynamics [9], a short pulse is necessary, since it allows one to disentangle the magnetic and electronic dynamics from nuclear vibrational dynamics. However, condensed matters are far more complex than atoms. The advantage of HHG over other tools has not been materialized, though using HHG to map bands has been proposed [10].

Recently, BaTiS$_3$ shows a broadband birefringence in infrared regions [11], but it is its quasi-one dimensionality and strong optical anisotropy that caught our attention. Low-dimensional materials with large oscillator strength are indispensable to nonlinear optical responses, if their band gaps ($E_g$) are small but nonzero. According to the well-known scaling rule, the third-order susceptibility $\chi^{(3)}$ is proportional to $\chi^{(3)} \propto E_g^{-6}$ [12, 13]. BaTiS$_3$ has a tiny gap, so even within a perturbation limit, its nonlinear susceptibility is expected to be strong, but little is known about its nonlinear optical properties, and even less its high-order harmonic generation.

In this paper, we predict strange high-order harmonics in hexagonal barium titanium sulfide (BaTiS$_3$) that circularly ($\sigma$) polarized light generates harmonics only at a few special orders. Regardless of laser pulse duration and photon energy, $\sigma$ light only induces first, fifth, seventh and eleventh harmonics, not third and ninth harmonics. We call them magic harmonics. Linearly ($\pi$) polarized light only generates normal odd-order harmonics. This finding is independent of whether the system has an inversion symmetry or not. Neither cubic nor tetragonal systems have magic harmonic orders even excited with $\sigma$ light. We carry out a detailed group symmetry analysis and find that magic harmonics are associated with the hexagonal group symmetry [14–17]. This group contains two subgroups: subgroup A contains the identity matrix and 180° rotation, and subgroup B includes the four proper
rotations, $C_6$, $C_6^2$, $C_6^4$, and $C_6^5$. Each subgroup only generates a normal harmonic spectrum, but if they both are present, they generate a destructive interference and exactly cancel out harmonics at the third and ninth orders. The same conclusion is found for the six improper rotations. Since cubic or tetragonal systems do not have such magic harmonics, magic harmonics found here present an opportunity to develop HHG into a possible structure characterization tool for phase transitions between hexagonal and nonhexagonal structures \[18\] in varieties of materials \[19\] \[28\]. Our finding complements the prior studies using linearly polarized light \[12\] \[29\] \[30\] well.

The rest of the paper is arranged as follows. In Sec. II, we outline our theoretical formalism. Our main results are presented in Sec. III, where we provide the details of our structural optimization, information of the electronic states, and high harmonic generations, followed by a symmetry group analysis. Finally, we conclude this paper in Sec. IV.

II. THEORETICAL FORMALISM

BaTiS$_3$ is a quasi-one dimensional material with Ti and S atoms forming a chain along the $c$ axis, with chain-chain distance of 6.749 Å. Figure II(a) shows its crystal structure. Ti chains pass through face-sharing sulfur octahedra. Figure II(b) shows its structure projected on to the $ab$ plane, where S atoms form a distinctive hexagonal motif and Ba atoms fill the empty space left behind. According to Huster \[31\] and Singh et al. \[11\], BaTiS$_3$ adopts a hexagonal BaNiO$_3$ structure with space group No. 194, P6$_3$/mmc. This structure has an inversion symmetry, with Ti at the Wyckoff position (2a), Ba at (2d) and S at (6h). Table II shows the Huster’s structure information. However, Niu et al. \[11\] suggested a different space group No. 186, P6$_3$mc, which has a lower symmetry without inversion symmetry and the number of symmetry operations is reduced from 24 to 12. Which structure, Niu’s or Huster’s, is more stable is an open question.

Theoretically, we employ the state-of-the-art density functional theory \[32\] to optimize the BaTiS$_3$ structure, with little input from the experiments. We first solve the Kohn-Sham equation \[32\] \[34\],

$$\begin{array}{c}
\left[-\frac{\hbar^2}{2m_e} \nabla^2 + V_{ne} + V_{ee} + V_{xc}\right] \psi_{ik}(\mathbf{r}) = E_{ik} \psi_{ik}(\mathbf{r}),
\end{array}$$

(1)

where $m_e$ is the electron mass, the terms on the left-hand side represent the kinetic energy, nuclear-electron attraction, electron-electron Coulomb repulsion and exchange correlation.
\( \psi_i k (r) \) is the Bloch wavefunction of band \( i \) at crystal momentum \( k \), and \( E_{ik} \) is the band energy. We include the spin-orbit coupling (SOC) using a second-variational method in the same self-consistent iteration \( [32] \), though we find the effect of SOC is very small. Wien2k \( [32] \) employs the linearized augmented planewave basis. In our calculation, the dimensionless product of planewave cutoff \( K_{\text{max}} \) and Muffin-tin radius \( R \) is \( RK_{\text{max}} = 9 \). Such a large value ensures that even higher eigenstates are accurately described. The Muffin-tin radius for each element is as follows, \( R_{\text{mt}}(\text{Ba}) = 2.5 \) Bohr, \( R_{\text{mt}}(\text{Ti}) = 2.32 \) Bohr, and \( R_{\text{mt}}(\text{S}) = 2.06 \) Bohr, so the core charges are confined within the spheres. We use a \( k \) mesh of \( 23 \times 23 \times 24 \), which is more than enough to converge our results.

To simulate HHG, we employ a laser pulse with duration 48 fs and photon energy 1.6 eV. These laser parameters are commonly used in experiments. We numerically solve the time-dependent Liouville equation for density matrices \( \rho_k \) at each \( k \) \( [33] \):

\[
\frac{i\hbar}{\partial t} \frac{\partial \rho_k}{\partial t} = [H, \rho_k],
\]

where \( H \) contains both the system Hamiltonian and the interaction between the laser and system. The expectation value of the momentum operator \( [3, 36] \) is computed from

\[
P(t) = \sum_k \text{Tr}[\rho_k(t) \hat{P}_k],
\]

where the trace is over band indices and crystal momentum \( k \). We include all the states from band 41 to 146 (see the arrows in Fig. \( [2] (a) \)), which cover the major portion of the energy spectrum. Calculations using different parts of the energy spectrum are also carried out, but there is no qualitative difference. To compute the harmonic signal, we Fourier transform \( P(t) \) to frequency domain (see details in Ref. \( [7] \)),

\[
P(\Omega) = \int_{-\infty}^{\infty} P(t) e^{i\Omega t} W(t) dt,
\]

where \( W(t) \) is the window function. Each component of \( P(\Omega) \) requires a separate Fourier transform. We find that the window function is necessary since small oscillations in \( P(t) \) at the end of the time window easily hide the harmonic structures at high orders. We emphasize that this window function does not alter the amplitude of the harmonic signal. We choose a hyper Gaussian \( W(t) = \exp[-b(at)^8] \), where \( a \) and \( b \) determine the width of the window function and the starting and ending times. In our current study, we use \( a = 0.035 / \text{fs} \) and \( b = 5 \times 10^{-9} \) (no unit), which spans the entire region of our data.
III. RESULTS

A. Structural optimization

Since earlier studies by Huster [31], structurally Niu and coworkers [11] provided two possible structures for BaTiS$_3$ with the same group symmetry. According to the international tables for crystallography [37], in group 186 (P6$_3$mc), Ti Wyckoff positions are at (2a): (0, 0, z) and (0, 0, z + 1/2), Ba positions are at (2b): (1/3, 2/3, z), (2/3, 1/3, z + 1/2), and S positions are at (6c): (x, −x, z), (x, 2x, z), (−2x, −x, z), (−x, x, z + 1/2), (−x, −2x, z + 1/2), (2x, x, z + 1/2). However, Niu’s positions [11] are not compatible with these positions. For instance, Niu’s second set of the S position is at (0.8301, 0.6603, 0.850), but it should be (0.8301, 0.1699, 0.350). Their y position can be reproduced by 2x − 1, where x is the x position; also one has to subtract 1/2 from their z position. In the following we first correct their Wyckoff positions and then carry out the calculation. Our Wyckoff positions are in compliance with the international tables for crystallography.

We optimize both their structures, and find that the first structure after optimization has a total energy lower than the second structure by 4 mRy. Both the structures have a lower energy than Singh’s structure. Our theoretical results support a structure with group symmetry P6$_3$mc. This is the first testable case for future experiments. Our theoretically optimized Wyckoff positions, together with the corrected experimental positions from Niu’s paper [11] are listed in Table II.

B. Electronic states

Before we present the high harmonic generation spectrum of BaTiS$_3$, we first investigate its electronic structures. Figure 2(a) shows our total density of states (DOS). The Fermi energy ($E_f$) is denoted by a dashed line. Consistent with Singh’s results ($E_g = 0.01$ eV) [11], our energy gap is very small, around $E_g = 0.014$ eV, on the energy scale of room temperature. We expect some important thermal-electric applications. Figure 2(b) shows the element-resolved partial density of states. We notice that Ba has a large contribution only in the lower energy window about 1 Ry below the Fermi level. Ti (dotted line) and S (dashed line) atoms dominate DOS around the Fermi level. The partial DOS for S is shown in Fig. 2(c), which is further resolved into different orbitals in Fig. 2(d). It is clear that the
states at -0.5 Ry are 3s states, while its 3p states are just around the Fermi level. As seen below, these states provide a channel for HHG.

C. High harmonic generation

We start with the structure with group symmetry P6$_3$/mmc [11, 31]. We align the laser polarization along the $x$ axis. Figure 3(a) shows the harmonic spectrum on a logarithmic scale as a function of harmonic orders. We see that all the harmonics appear at odd orders along the $x$ axis, which is the original laser polarization direction. The signals along the $y$ and $z$ axes are at the noise level and not shown. Next, we use Niu’s experimental structure with group symmetry P6$_3$mc. Figure 3(b) shows that under the same laser condition, the harmonic signals along the $x$ axis for these two structures are identical (compare Figs. 3(a) and (b)), where all the harmonics are at odd orders. However, qualitative differences are observed along the $z$ axis. P6$_3$mc has no inversion symmetry and harmonics along the $z$ axis appear at even orders. This agrees with the symmetry properties with this group symmetry [15, 17] that the even orders only appear when the laser polarization is along the $z$ axis. Consistent with Niu’s observation of strong optical anisotropy [11], our zeroth-order harmonic signal along the $c$ axis is particularly strong; and to obtain clean harmonics at high orders, we subtract $P(-\infty)$ from $P(t)$ before we compute the power spectrum shown in Fig. 3(b). This is our second testable result: If Huster’s structure is correct, no harmonic signal along the $z$ direction is present; if Niu’s structure is correct, even harmonics along the $z$ axis appear.

The structural symmetry is not the only information that HHG can reveal. When we employ circularly polarized light ($\sigma$), to our surprise, some harmonics are mysteriously missing. Figure 4(a) shows that the third and ninth harmonics disappear. Only the 1st, 5th, 7th, and 11th harmonics remain, magic harmonics. To the best of our knowledge, this has never been reported before. These magic harmonics do not depend on whether the group symmetry is P6$_3$/mmc (Fig. 4(a)) or P6$_3$mc (Fig. 4(b)). Therefore, the common symmetry operations shared by these two space groups must be at the root of these magic harmonics. However, since we have a huge number of $k$ points, it is a challenge to determine the origin of these magic harmonics. We decide to select a single $k$ point and resolve $P_k(t)$ according
to its 12 symmetry operations

$$P_k(t) = \sum_{s=1}^{6} P^s_k(t) + \sum_{q=1}^{6} P^q_k(t)$$  \hspace{1cm} (5)

where \(s\) refers to six proper rotations (see Fig. \(\Pi\)(c)) and \(q\) runs over six improper rotations (reflections) (Fig. \(\Pi\)(d)). We symmetry-resolve \(P_k(t)\), not its Fourier transformed \(P_k(\omega)\), because the interference only occurs in the time domain, not in the frequency domain.

Equation (5) is seemingly simple, but harbors too many possible combinations, \(\sum_{i=1}^{12} \binom{i}{12}\). Lax [38] has an example of an equilateral triangle, with six symmetry operations. His example can not directly apply to our problem, but we notice that in his diagram the triangle has a mirror plane which could cancel all the even-order harmonics. This motivates us to lay out all the proper rotations within the \(ab\) plane (Fig. \(\Pi\)(c)), where we label each vertex with a symmetry operation. \(C^3_6\) is a 180° rotation with respect to the \(c\) axis, much like an inversion operation in the Lax’s example. We immediately recognize that the identity matrix \(E\) and rotation \(C^3_6\), or subgroup A below, ensure that even harmonics do not appear. This is verified by our calculation (see Fig. \(\Pi\)(c)), but their harmonics are normal, and no magic orders are observed. Note that the disappearance of the even harmonics does not contradict the symmetry properties because the even harmonics allowed by the symmetry \(P_{63}mc\) appears only when the electric field is along the \(z\) axis [15, 17]. In our case, our laser field polarization is in the \(xy\) plane. Experimentally, Ghimire et al. [6], who employed linearly polarized in the \(ab\) plane, also found no even order harmonics for \(ZnO\) which happens to have the same group symmetry \(P_{63}mc\). Therefore, our results are fully consistent with the symmetry requirement and prior experiments [6].

What about the remaining four proper rotations or subgroup B? If we compare Figs. \(\Pi\)(b) and \(\Pi\)(c), we notice that these symmetry operations bring \(S\) atoms to their equivalent positions while keeping \(Ti\) atoms intact. These four rotation matrices are

$$C^6_{6}(60^\circ) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \hspace{1cm} C^2_{6}(120^\circ) = \begin{pmatrix} \frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix},$$  \hspace{1cm} (6)

$$C^4_{6}(240^\circ) = \begin{pmatrix} -\frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}, \hspace{1cm} C^5_{6}(300^\circ) = \begin{pmatrix} \frac{1}{2} & -\frac{\sqrt{3}}{2} & 0 \\ \frac{\sqrt{3}}{2} & \frac{1}{2} & 0 \\ 0 & 0 & 1 \end{pmatrix}. \hspace{1cm} (7)$$
We first check whether each pair of symmetry operations lead to magic harmonics, but this fails, so we simply combines all of them. The results are shown Fig. 4(d), where all the harmonics appear normal. Then we test whether mixing some improper rotations could cause magic harmonics, but unsuccessful. We also examine the prior results in magnetic monolayers with tetragonal symmetries [7], but we do not find any magic harmonics under the same laser condition. After a long and difficult testing, we finally come to realize that the summation over all \( P_s(t) \) of the proper rotation might be able to reveal magic harmonics, and to our amazement, it indeed works. Figure 4(e) shows magic harmonics, with the third and ninth order harmonics missing. It is the destructive interference between two symmetry subgroups A and B that leads to magic harmonics. It is an easy task to extend this finding to improper rotations (see Fig. 4(d)). Different from the proper rotations, the mirror image operations \( \sigma_{yz} \) and \( \sigma_{xz} \) form a subgroup, with the four remaining operations from \( \sigma_1 \) to \( \sigma_4 \) forming another subgroup. These two subgroups play the same role as the two subgroups for the proper rotations. Once we add their contributions up, we again reproduce the magic harmonics. We also examine other hexagonal systems and reach the same conclusion. These magic harmonics are a hallmark of hexagonal structure, which is likely to have important applications in the future. For instance, hexagonal-cubic crystal structure transformation was found in many technologically important materials, aluminum nitride [19], GaN [20], BN [21, 22], zinc oxynitride layers [24], NaYF \(_4\) [25], Eu\(_2\)O\(_3\) [26], CdTe [27] and others [28]. Our finding suggests a simple protocol to determine whether a hexagonal-cubic phase transition occurs by checking whether these magic harmonics appear.

IV. CONCLUSION

We have demonstrated magic high-order harmonics in hexagonal and quasi-one dimensional solid BaTiS\(_3\). Our results reflect the usefulness of group theory and power of high harmonic generation as a structural characterization tool. Specifically, we show how harmonics are generated sensitively depends on crystal structures and laser polarization. Whether BaTiS\(_3\) adopts P6\(_3\)mmc or P6\(_3\)mc symmetry determines whether even order harmonics appear along the \( c \) axis. The qualitative difference is found under circularly (\( \sigma \)) polarized light excitation between the hexagonal structure for BaTiS\(_3\) and tetragonal structure [7]. \( \sigma \) light produces no magic harmonics in tetragonal systems, but it generates magic harmonics.
in hexagonal systems. These magic harmonics are the hallmark of the hexagonal structure, and potentially provide a tool to investigate phase transitions in a wide scope of materials. One ideal system to realize our prediction could be BaVS$_3$. At room temperature BaVS$_3$ adopts P6$_3$/mmc symmetry, but transforms to an orthorhombic structure between 70 K and 240 K [39]. Therefore, our finding will motivate experimental and theoretical investigations in other research fields.

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TABLE I. Wyckoff positions of BaTiS\textsubscript{3} determined by Huster\textsuperscript{[31]}. His structure is of BaNiO\textsubscript{3}-type and has symmetry group No. 194, P\textit{6}\textsubscript{3}/mmc. This structure has an inversion symmetry. The lattice constants are \(a = 6.756(1)\text{Å}\) and \(c = 5.798(1)\text{Å}\).

| Atom Position | \(x\)  | \(y\)  | \(z\)  |
|---------------|-------|-------|-------|
| Ti            | 2a    | 0     | 0     |
| Ba            | 2d    | \(\frac{1}{3}\) | \(\frac{2}{3}\) | \(\frac{3}{4}\) |
| S             | 6h    | 0.1655(10) | 0.3310(10) | 1/4 |

TABLE II. Optimized Wyckoff positions of BaTiS\textsubscript{3}, with group No. 186, P\textit{6}\textsubscript{3}mc and lattice constants \(a = 6.749\text{Å}\), \(b = 6.749\text{Å}\), and \(c = 5.831\text{Å}\). S atoms are at 6\textit{c} positions \((x, -x, z), (x, 2x, z), (-2x, -x, z), (-x, x, z + \frac{1}{2}), (-x, -2x, z + \frac{1}{2}), (2x, -x, z + \frac{1}{2})\). This structure has no inversion symmetry. The experimental results from Niu \textit{et al.}\textsuperscript{[11]} are shown in the parenthesis. If there is no difference between their experiment and our theory, only one entry is listed.

| Atom Position | \(x\)  | \(y\)  | \(z\)  |
|---------------|-------|-------|-------|
| Ba            | 2b    | \(\frac{1}{9}\) | \(\frac{2}{9}\) | 0.2989 (0.298) |
| Ti            | 2a    | 0     | 0     | 0.5067 (0.522) |
| S             | 6c    | 0.8329 (0.8301) | 0.1671 (0.1618) | 0.2875 (0.298) |

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FIG. 1. High harmonic generation in BaTiS$_3$. (a) Unit cell of BaTiS$_3$ with group symmetry P6$_3$mc has no inversion symmetry. The laser polarization can be either in the $xy$ ($ab$) plane or along the $z$ ($c$) axis. Harmonics can be detected by a camera. (b) The same structure projected in the $ab$ plane, with two units along the $a$ and $b$ axes. (c) Six symmetry rotations in the $ab$ plane can be separated into two subgroups A ($E$, $C^3_6$) and B ($C_6$, $C^2_6$, $C^4_6$, $C^5_6$). These two subgroups are the cause of magic harmonics. (d) Six improper rotations can also be categorized into two subgroups A ($\sigma_{yz}$, $\sigma_{xz}$) and B ($\sigma_1$, ..., $\sigma_4$).
FIG. 2. (a) Total density of states (DOS). The arrows highlight the excitation process of our laser pulse. States from 41 to 146 are included in our calculation. The Fermi level is denoted by a horizontal dashed line. (b) Element-resolved partial DOS, where the states around the Fermi level are dominated by Ti and S atoms. (c) Partial density of states for sulfur, which is further decomposed into different orbital characters in (d).
FIG. 3. (a) Logarithmic of high harmonic spectrum as a function of harmonic order under \(x\)-linearly polarized laser excitation. The crystal structure has group symmetry P6\(_3\)mmc and has inversion symmetry. All the harmonics along the \(x\) axis are odd orders. Signals along the other axes are at noise level. (b) Harmonic signals for the same laser pulse but for the structure with group symmetry P6\(_3\)mc. This structure has no inversion symmetry, so the even order harmonics appear along the \(c\) (\(z\)) axis (dashed line). The signal along the \(x\) axis is similar to (a). The \(z\) component of harmonics without treatment is shown on the top. Since the signal along the \(z\) axis is too strong, we subtract its initial value \(P(-\infty)\) from \(P(t)\) and then carry out the Fourier transformation to get a “cleaner” spectrum labeled with “\(z\) (subtracted)”. Even harmonic only appears when the laser polarization is along the \(z\) axis [15, 17].
FIG. 4. (a) Magic high-order harmonics generated from BaTiS₃ with P₆₃/mmc symmetry under circularly polarized light (σ) in the xy plane, where third and ninth harmonics are missing. The light polarization plane is within the ab plane (see Fig. 1(b)). Note that the x and y components are indistinguishable within numerical accuracy. (b) Magic harmonics are also present in BaTiS₃ with a symmetry group P₆₃mc without inversion symmetry. (c) High-order harmonics at a crystal momentum point close to (0.05, 0.05, 0). The results are similar for other k points. The summation is over symmetry operations in subgroup A (E and C₃). The harmonics are normal. (d) Same as (c), but the summation is over symmetry elements in subgroup B (C₆, C₂, C₄, C₅). These symmetry rotations keep Ti atoms intact while transforming S atoms into their equivalent positions (see Figs. 1(b) and 1(c)). The harmonics are also normal and appear only at odd orders. (e) Summation of all the proper rotations on HHG signal reproduces magic harmonics seen in (a) and (b). It is the destructive interference between these two subgroups that cancels the third and ninth harmonics.