Classification of second harmonic generation effect in magnetically ordered materials

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The relationship between magnetic order and the second harmonic generation (SHG) effect is a fundamental area of study in condensed matter physics with significant practical implications. In order to gain a clearer understanding of this intricate relation, this study presents a comprehensive classification scheme for the SHG effect in magnetically ordered materials. This framework offers a straightforward approach to connect magnetic order and SHG effect. The characteristics of the SHG tensors in all magnetic point groups are studied using the isomorphic group method, followed by a comprehensive SHG effect classification scheme that includes seven types based on the symmetries of the magnetic phases and their corresponding parent phases. In addition, a tensor dictionary containing the SHG and linear magneto-optic (LMO) effect is established. Furthermore, an extensive SHG database of magnetically ordered materials is also built up. This classification strategy exposes an anomalous SHG effect with even characteristic under time-reversal symmetry, which is solely contributed by magnetic structure. Moreover, the proposed classification scheme facilitates the determination of magnetic structures through SHG effect.

INTRODUCTION

Symmetry plays a crucial role in determining the physical properties of matter. In magnetically ordered materials (such as ferromagnetic (FM) materials, antiferromagnetic (AFM) materials, ferrimagnetic materials, etc.), the spin directions of electrons are arranged in orderly fashions, leading to spontaneous time-reversal symmetry breaking and rich physical phenomena. To reveal the symmetries of magnetically ordered materials, optical technical is usually considered as an effective approach [1–3]. The linear magneto-optic (LMO) effect (refers specifically to the Faraday effect [4] in transmission and Kerr effect [5] in reflection here) and the second harmonic generation (SHG) effect are two basic and complementary optical tools to study magnetic structures in experiments. SHG effect is particularly powerful in characterizing AFM materials where the LMO method fails, particularly in recent two-dimensional (2D) AFM materials, for example, bilayer CrI3 [6], MnPS3 [7], MnPSe3 [8], CrSBr [9] and NiI2 [10]. Therefore, SHG is widely adopted to detect magnetic phase transitions [11–15], magnetic symmetries, magnetic orders [16–18] and domain structures [13, 14, 19], due to its spectral and spatial resolution. Therefore, bridging the connection between the SHG effect and magnetic order is a frontier area in this field [12, 13].

Comprehensively classifying the SHG effect in magnetically ordered materials offers a promising approach to better understand the intriguing relationship between the SHG effect and the magnetic structures. However, achieving this goal is still elusive. It is well-known that the appearance of the SHG effect may indicate the breaking of inversion symmetry under the electric dipole approximation. In magnetically ordered materials, the inversion-symmetry-breaking can be induced by either asymmetric crystal structures (inversion symmetry breaking resulting from the parent crystallographic structures) or magnetic structures [20–26]. Birss, in the 1960s [27, 28], divided SHG tensor elements into two types based on their parities under time-reversal symmetry: t-type (even with time-reversal symmetry $T$) and c-type (odd with time-reversal symmetry $T$). Until now, this two-category classification is widely used [6–9, 11, 12]. However, the classification faces daunting challenges in distinguishing whether the inversion symmetry breaking. Furthermore, the SHG classification is not mutually exclusive and spatial symmetry is not considered, leading to the complexity in characterizing the SHG effect. Moreover, the unsystematic study of all magnetic groups may lead to some misconceptions. For example, the SHG effects in magnetically ordered materials are assumed to be odd with time reversal symmetry [6–10], since the magnetic structure is reversed under the time-reversal operator. However, it should be noted that the even SHG tensors can also be induced by magnetic order individually because no symmetry prohibits them, and this anomalous SHG effect has not been realized in previous literature. Therefore, a comprehensive SHG classification that reveals the characteristics of SHG effect and accurately identifies the origin of the inversion symmetry breaking, whether it arises from crystallographic or magnetic structures is highly desirable.

In this study, we introduce an SHG classification method in magnetically ordered materials containing...
we use the isomorphic group method to transform the SHG tensor under the magnetic point groups into nonmagnetic point groups, thereby revealing the rules governing the SHG tensor. Based on this, we classify the SHG effect into seven types based on the symmetries of the magnetic phases and parent phases. Additionally, we build up a tensor dictionary containing the SHG and LMO effects and establish a comprehensive classification for the magnetically ordered materials in the MAGNADATA database [29]. Furthermore, our classification strategy predicts an anomalous SHG effect, which exhibits even characteristic with time reversal symmetry and contributed by magnetic structure solely. The first-principles calculations on some representative magnetically ordered materials confirm the effectiveness of the proposed classification.

RESULTS

Characteristics of SHG tensors of all magnetic points groups with isomorphic group method

Typically, SHG susceptibility tensors can be divided into T-even (i-type, $\chi_{ijk}^{\text{even}}$) and T-odd (c-type, $\chi_{ijk}^{\text{odd}}$) parts [27, 28],

$$\chi_{ijk}^{(2)} = \chi_{ijk}^{\text{even}} + \chi_{ijk}^{\text{odd}}. \quad (1)$$

The subscript $i$ ($j$ and $k$) denotes the direction of second-order polarization (fundamental incident) of light. The notation of the SHG tensor is presented in Supplementary Notes 1.1 and 3.2.

According to Neumann’s principle [27, 30–32], the SHG tensors are constrained by the magnetic point groups (MPGs, denoted as $M_0$) rather than the magnetic space groups (MSGs, denoted as $M$, also known as Shubnikov groups) [33–35]. The point group operations in MPGs contain two categories: the unitary point operators $R$, which do not involve the time operation, such as rotation operation $n$ and rotation-inversion operation $\tilde{n}$ (n=1, 2, 3, 4, 6), and the anti-unitary point operation $R'$. The relationship between $R$ and $R'$ is described as $R' = TR$, where $T$ is the time reversal symmetry. The MPGs can be divided into three classes based on the presence of the $R$ and $R'$: (a) original MPGs, which are constituted by ordinary point groups $G_0$ and lack any anti-unitary operators $R'$, i.e. $M_0 = G_0$, (b) grey MPGs, in the form of $M_0 = G_0 + TG_0 = G_0 + 1'G_0$ ($1' = 1T$ also means the $T$ symmetry), (c) black-white (BW) MPGs $M_0 = S_0 + T(G_0 - S_0) = S_0 + R'S_0$, where $S_0$ is a halving subgroup of $G_0$. A brief introduction to MPGs and MSGs is provided in Supplementary Note 1.2.

The transformations of the even and odd SHG tensors under a unitary point operation $R$ can be expressed as follows:

$$R : \chi_{ijk}^{\text{even/odd}} = \sum_{lmn} R_{il} R_{jm} R_{kn} \chi_{lmn}^{\text{even/odd}}, \quad (2)$$

where $R_{ij}$ represents an element of the 3x3 matrix for the unitary point operation $R$. According to Eq. (2), the transformations of the even and odd SHG tensors, i.e., $\chi_{ijk}^{\text{even}}$ and $\chi_{ijk}^{\text{odd}}$, are identical under $R$, since $R$ does not contain the time-reversal operation $T$. However, the signs of $\chi_{ijk}^{\text{even}}$ and $\chi_{ijk}^{\text{odd}}$ are opposite under the transformations of the anti-unitary point operation $R'$:

$$R' : \chi_{ijk}^{\text{even/odd}} = \pm \sum_{lmn} R_{il} R_{jm} R_{kn} \chi_{lmn}^{\text{even/odd}}. \quad (3)$$

The plus and minus sign in Eq. (3) correspond to the even part ($\chi_{ijk}^{\text{even}}$) and the odd part ($\chi_{ijk}^{\text{odd}}$) of SHG tensors, respectively [31].

Generally, the characteristics of SHG tensors under all MPGs can be directly obtained by solving the above linear algebra equations with the aid of invariant theory (see Refs. [27, 30, 31] and “Bilbao Crystallographic Server/MTENSOR” website). However, the SHG tensor characteristics in magnetically ordered materials are more complicated than that of non-magnetically ordered materials. Currently, the relationships between MPGs and SHG tensors as well as the rules governing the SHG effect under all MPGs have not been clearly established. This lack of understanding hinders the study of the SHG effect.

Here, we investigate the SHG tensors using the isomorphic group method. In group theory, $-1$ is equivalent to the inversion operator $I$, because $-1 = -I_0 I_0 = I_0$ is the identity matrix and $-I_0$ is the matrix of the inversion operation. Therefore, the transformation of $\chi_{ijk}^{\text{odd}}$ in Eq. (3) under the anti-unitary point operation $R'$ can be re-written as follows:

$$R' : \chi_{ijk}^{\text{odd,even}} = -\sum_{lmn} R_{il} R_{jm} R_{kn} \chi_{lmn}^{\text{odd,even}} = \sum_{lmn} (-R)_{il} (-R)_{jm} (-R)_{kn} \chi_{lmn}^{\text{odd}}$$

$$= \sum_{lmn} (IR)_{il} (IR)_{jm} (IR)_{kn} \chi_{lmn}^{\text{odd}}. \quad (4)$$

The above equation implies that the constraint imposed by the anti-unitary point operation $R'$ on $\chi_{ijk}^{\text{odd}}$ is equivalent to an unitary point operation $R$ times an inversion operation $I$, i.e. $IR$.

The set of all the unitary and anti-unitary $R'$ operations in a specific magnetically ordered material constitute a closed MPG. The transformations of $\chi_{ijk}^{\text{odd}}$ under all the unitary point operations $R$ ($R \in S_0$) and anti-unitary point operations $R'$ ($R' \in R'S_0$) of a BW MPG $M_0$ are equivalent to $S_0$ and $IR'S_0$, respectively. Thus, the symmetry restrictions imposed by a BW MPG $M_0$ on $\chi_{ijk}^{\text{odd}}$ is equivalent to a nonmagnetic point group (PG) $G_1$ ($S_0 + IR'S_0$). Similarly, the symmetry constraint of $\chi_{ijk}^{\text{even}}$ imposed by a BW MPG $M_0$ is equivalent to a
nonmagnetic PG $G_0 = S_0 + R S_0$, because the transformations of $\chi^{\text{even}}_{ijk}$ under $R$ and $R'$ are identical, as indicated in Eq. (2) and Eq. (3). Because $M_0$, $G_0$ and $G_1$ are isomorphic groups, this implies the isomorphic group method can be employed to transform the SHG tensor under MPGs into nonmagnetic PGs.

As depicted in Fig. 1, we utilize two nonmagnetic isomorphic PGs, $G_0$ and $G_1$, to determine the characteristics of the even ($\chi^{\text{even}}_{ijk}$) and odd ($\chi^{\text{odd}}_{ijk}$) SHG tensors under a BW MPG $M_0$, respectively. The SHG tensors of grey and original MPGs can also obtained using the above isomorphic group method, which are given in Supplementary Note 1.3. No additional numerical calculations are needed, since the characteristics of the SHG tensors of all the nonmagnetic PGs can be found in general nonlinear optics textbooks [36, 37]. Importantly, the isomorphic group method elucidates the rules governing the SHG tensors [27, 30, 31].

The characteristics of LMO effect in all MPGs are also studied in Supplementary Note 2. In our work, LMO effect specifically refers to the Faraday effect [4] and Kerr effect [5], both of which belong to the linear optics. These two kinds of LMO effects arise from the magneto-circular dichroism in transmission (Faraday effect) or reflectivity (Kerr effect) of polarized light in magnetically ordered materials. It was once believed that LMO effect could only exist in magnetically ordered materials with nonzero net magnetization. However, with the the permitted symmetries, LMO effect has been theoretically predicted or experimentally observed in AFM materials with net magnetization [38]. Specific examples include collinear AFM materials (such as RuO$_2$ [39–41] and MnTe [42]), coplanar but non-collinear AFM materials (such as Mn$_3$X (X = Rh, Ir, Pt) [43], Mn$_3$Y (Y = Ge, Ga, Sn) [44–46] and Mn$_3$Zn (Z = Ga, Zn, Ag, Ni) [47]), as well as in non-coplanar AFM materials (such as $\gamma$-Fe$_{0.5}$Mn$_{0.5}$ [48] and K$_{0.5}$RhO$_2$ [48]). In all, LMO effect can exist in magnetically ordered materials with permitted MPGs. The higher order magneto-optic effects, such as spontaneous nonreciprocal optical effect [49–52] and the magneto-birefringence effect [53] (Voigt effect [54] and Cotton-Mouton effect [55]), are not investigated in our work.

As stated in the introduction, the LMO and SHG effects are two complementary optical methods to study the magnetically ordered materials. The characteristics of SHG and LMO effects in all MPGs are listed in Supplementary Note 3, which provides a dictionary for characterizing the magnetic structures with these two optical techniques in experiments. Moreover, this isomorphic group method is also suitable for other tensors in magnetic systems, such as circular photo-galvanic effect (CPGE) whose susceptibilities comprise 3×3 pseudo-tensors (see Supplementary Note 4 for detail). This indicates that this method is a powerful tool for studying the tensors in magnetic systems.

According to our symmetry analysis, the SHG tensors in all MPGs can be divided into four cases based on their characteristics: (1) original MPGs without inversion symmetry, (2) grey MPGs without inversion symmetry, (3) BW MPGs without inversion symmetry but with PT symmetry (combination of time-reversal $T$ and spatial inversion $P$ symmetry), and (4) BW MPGs without inversion symmetry nor PT symmetry. The MPGs and the corresponding SHG characteristics are listed in Table I. Only even SHG tensors exist in grey MPGs (Case 2). Only the odd SHG tensors exist in BW MPGs with PT symmetry (Case 3). In original MPGs without inversion symmetry (Case 1) and BW MPGs without $P$ or $PT$ symmetry (Case 4), both the odd and even SHG tensors exist. $\chi^{\text{even}}_{ijk}$ and $\chi^{\text{odd}}_{ijk}$ are the same in Case 1. However, $\chi^{\text{even}}_{ijk}$ and $\chi^{\text{odd}}_{ijk}$ differ in Case 4 as they are constrained by different isomorphic PGs ($G_0$ and $G_1$). Table I provides a clear and concise summary of the SHG behavior for different MPGs, which reveals the rules governing the SHG effect under all MPGs.

**Classification of the SHG effect in magnetically ordered materials**

Next, we classify the SHG effect in magnetically ordered materials based on the symmetries of magnetic and parent structures to reveal the characteristics of SHG effect further. In view of the fact that breaking the inversion symmetry could arise from either crystallographic or magnetic structure, we should also take the symmetry of the parent phase into account in addition to the mag-

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**FIG. 1. Diagram of the isomorphic group method to analyze the characteristic of SHG tensor.** The transformations of $\chi^{\text{even}}_{ijk}$ and $\chi^{\text{odd}}_{ijk}$ under a BW MPG $M_0$ ($= S_0 + R S_0$) are equivalent to those under nonmagnetic PGs $G_0 = S_0 + R S_0$, top panel) and $G_1 = S_0 + I R S_0$, bottom panel), respectively. $S_0$ is a halving subgroup of MPG $M_0$. $R$ is a unitary point operation, $R'$ is an anti-unitary point operation, and $I$ is the inversion operation. Further information is available in Supplementary Note 1.
TABLE I. Characteristics of SHG tensors in all MPGs without inversion symmetry.

| SHG cases | Even SHG tensor | Odd SHG tensor | MPGs |
|-----------|----------------|----------------|------|
| Case 1. Original MPG without P (20) | $\chi_{ijk}^{\text{even}}(G_0)$ Same as odd | $\chi_{ijk}^{\text{odd}}(G_0)$ Same as even | 1(M), 2(M), m(M), 222, mm2, 4(M), 4(M), 422, 4mm, 42m, 3(M), 32, 3m, 6(M), 6(M), 622, 6mm, 6m2, 23, 43m |
| Case 2. Grey MPG without P (20) | $\chi_{ijk}^{\text{even}}(G_0)$ ✓ | × | 11′, 21′, m1′, 2221′, mm21′, 41′, 41′, 4221′, 4mm1′, 42m1′, 31′, 321′, 3m1′, 61′, 61′, 6221′, 6mm1′, 6m21′, 23′, 43m1′ |
| Case 3. BW MPG without P but with PT (20) | × | $\chi_{ijk}^{\text{odd}}(S_0)$ ✓ | $\chi_{ijk}^{\text{odd}}(S_0)$ |
| Case 4. BW MPG without P nor PT (27) | $\chi_{ijk}^{\text{even}}(G_0)$ ✓ | $\chi_{ijk}^{\text{odd}}(G_1)$ Different with odd | $\chi_{ijk}^{\text{odd}}(G_1)$ Different with even |

1 The corresponding SHG tensors are presented in Supplementary Note 3.
2 The numbers in the first column represent the number of MPGs exhibiting the SHG effect.
3 The letter “M” in the bracket of the fourth column indicates the MPG permitting the LMO effect.

FIG. 2. Flow chart for SHG classification scheme in magnetically ordered materials. First, the MPGs are determined from the MSGs of magnetically ordered materials. Then, the SHG tensors are further divided into four cases based on the symmetries of MPGs (refer to Table I). Finally, the types of SHG effect in magnetically ordered materials are determined based on whether the parent phases possess inversion symmetry (wP) or not (woP). In this notation, $M$ represents the MSG, and $G$ in the last judging rhombus denotes the space group (SG) of the parent phase. The colored parallelograms on the right indicate the types of SHG effect. The letter “G” in G-wP and G-woP denotes the grey MPG, and the letter “O” in O-wP and O-woP represents the original MPG. Similarly, “BW” in BW-wP and BW-woP represents the BW MPG without PT symmetry, and “PT” in PT-wP indicates the BW MPG with PT symmetry. Note that MPGs of 432, 4321′, and $m^3/m’$ are excluded because their symmetries forbid the emerge of SHG effect, even though inversion symmetry is broken.

① except 432. ② except 4321′. ③ except $m^3/m’$. ④ × indicates the case PT-woP do not exist
magnetic phase, similar to the classification in species of ferromagnetic, ferroelectric and ferroelastic crystals [56]. In magnetically ordered materials, the parent phases usually exhibit higher symmetry than the magnetic phases. As a consequence, the inversion symmetry broken in the magnetic phases could still be retained in the parent phases. Therefore, each case in Table I could be further divided into two subcases, depending on whether parent phases possess inversion symmetry (wP, i.e. with inversion symmetry) or not (woP, i.e. without inversion symmetry). An exception arises in Case 3, as the parent phases must possess the inversion symmetry $P$ if the MPGs exhibit $PT$ symmetry. Figure 2 depicts the flow chart of the SHG classification scheme. Table II presents the seven types of SHG effect, labeled as $O$-wP, $O$-woP, $G$-wP, $G$-woP, $PT$-wP, $BW$-wP, and $BW$-woP, along with their corresponding characteristics. Because of encompassing all possible SHG cases in magnetically ordered materials, this classification is exhaustive and mutually exclusive.

Figure 2 and Table II present a straightforward but practical classification approach. Additionally, the outcomes presented in Table II offer valuable insights into the distinct roles of magnetic structures and crystallographic structures in SHG effect. In other words, this classification strategy reveals the symmetries (containing crystallographic and magnetic symmetries) and physical mechanisms underlying the SHG effect in magnetically ordered materials. For example, magnetically ordered materials with inversion symmetry in their parent phases exhibit four distinctive types of SHG effects, namely, $O$-wP, $G$-wP, $PT$-wP and $BW$-wP. All these types of SHG effects arise from magnetic structure rather than crystal asymmetry. In particular, the $G$-wP type SHG effect is solely contributed by magnetic structures, and only even SHG tensors are present, which has not yet been explored before. In contrast, only three possible SHG types are anticipated in magnetically ordered materials without inversion symmetry in their parent phases, namely $O$-woP, $G$-wP and $BW$-woP. The even SHG tensors of these three SHG types arise from crystal and magnetic structures, while the odd SHG tensors solely originate from magnetic structure. This comprehensive classification is superior to the two-category classification (c-type and i-type) [27, 28], since it provides a clearer understanding of the relationship between symmetry and SHG effect.

Now we apply this classification method to real materials. MAGNDATA [29] in the Bilbao Crystallographic Server (BCS) is a well-known material database that encompasses over 1795 magnetic structures. It is worth noting that we refer them to magnetic structures, since one material may possess several magnetic structures. After excluding the incommensurate magnetic structures (the magnetic lattice constants are not integer multiples of those of parent phases) [57], there are 1655 magnetic structures remaining with BCS-ID (identity number in MAGNDATA of BCS) ranging from 0.1-0.835, 1.0.1-1.0.52, 1.1-1.663, 2.1-2.86 and 3.1-3.19. The corresponding materials are listed in Supplementary Table XI. After removing duplicate data, there are 1432 magnetic structures left. Using the process presented in Fig. 2, the SHG effect of each magnetic structure can be classified, as shown in Fig. 3. We find that 496 magnetic structures process the SHG effect, and 451 magnetic structures exhibit the LMO effect. Out of the 496 magnetic structures with SHG effect, 100 of them also have LMO effect. The 496 magnetic structures with SHG effect can be further categorized into the above seven types, as illustrated in Fig. 3b. The clarification of the SHG and LMO effects for all magnetic structures in MAGNDATA is compiled into a database which is presented in Supplementary Note 6.

**FIG. 3.** Statistics on the SHG types in the MAGNDATA database. (a) Counting of materials with SHG and LMO effects in the 1432 magnetic structures (removing duplicate data). (b) Classification of the 496 magnetic structures with SHG effect. The detailed information of every material is presented in Supplementary Note 6.

Guided by this classification, we will discuss two examples to validate our isomorphic theory and classification method. The first one involves $VB{Br_3}$, which suggests that the magnetic structure can induce the even-time-reversal SHG tensors individually. In the second example, we will study the SHG effect in AFM materials $R{MnO_3}$ ($R = Sc, Y, In, Dy, Ho, Er, Trm, Yb$ and Lu) with diverse magnetic
TABLE II. Classification of the SHG effect based on the symmetries of magnetic structures (i.e. MPGs and MSGs) and parent structures (i.e. parent SGs).

| MPGs / MSGs | Parent SGs | With inversion symmetry (wP) | Without inversion symmetry (woP) |
|-------------|------------|-----------------------------|---------------------------------|
| Case 1. Original MPGs (O) without inversion symmetry (Type-I MSGs) | O-wP | Even/odd: from magnetic structure | O-woP |
| Case 2. Grey MPGs (G) without inversion symmetry (Type-IV MSGs) | G-wP | Even: from magnetic structure | G-woP |
| Case 3. BW MPGs with PT symmetry (PT) (Type-III MSGs) | PT-wP | Odd: from magnetic structure | × Not possible |
| Case 4. BW MPGs without PT nor P symmetry (BW) (Type-III MSGs) | BW-wP | Even/odd: from magnetic structure | BW-woP |

1 A brief introduction of MPGs and MSGs is provided in Supplementary Note 1.2.
2 The type-II MSGs describe the nonmagnetically ordered materials with time-reversal symmetry, which are beyond the scope of our study, and therefore are not included.
3 “Crystal asymmetry” refers to inversion symmetry breaking resulting from the parent crystal structure.

![Figure 4](image)

FIG. 4. Calculation results of VBr$_2$. (a) Crystal structure of parent phase of bulk VBr$_2$ (upper panel: side view, lower panel: top view). (b) Magnetic structure (upper panel: side view, lower panel: top view), (c) band structures and (d) nonzero SHG susceptibilities of in-plane frustrated bulk VBr$_2$. (e) The odd SHG susceptibilities of bulk VBr$_2$ whose interlayer magnetic moments are parallel aligned. The SOC strength is increased by an order of magnitude to make the odd part of SHG susceptibilities more significant. (f) Magnetic structure (side view), (g) band structures and (h) nonzero SHG susceptibilities of bilayer VBr$_2$ with A-type AFM magnetic structure. The black rhombuses in (a) and (b) mean the unit cell and magnetic unit cell, respectively. The “+” and “−” signs in (d), (e) and (h) denote the positive and negative magnetic structures.

structures.

Example 1: Anomalous SHG in bulk VBr$_2$

It was previously presumed that SHG effect induced by magnetic structure would reverse upon switching the magnetic order due to the inherent oddness of magnetic order under time reversal symmetry. Here, we present a
typical example violating such assumption in bulk VBr$_2$ [58–60]. As depicted in Fig. 4a, the parent phase of bulk VBr$_2$ processes the inversion symmetry (SG: P3m1), and one V atom has six nearest V atoms forming equilateral triangles. Therefore, in-plane geometrical frustration is expected accompanying with the inversion symmetry breaking when the magnetic interactions are antiferromagnetic, as illustrated in Fig. 4b. Additionally, the magnetic moments of the adjacent interlayer V atom are opposite to each other, resulting to the two adjacent layers be connected by Tc/2 symmetry. Its MSG is P$\bar{6}$c31c (P$_{\bar{6}}$c means the BW Bravais lattices), as presented in Fig. 4b. According to the classification rule, the SHG type of bulk VBr$_2$ is classified as G-wP, which is induced by the magnetic structure and it is even under time-reversal symmetry.

The band structures of bulk VBr$_2$ are shown in Fig. 4c. The bands split because of the breaking inversion symmetry and PT symmetry, and the band energies of +k and −k points are equivalent due to the “effective” time-reversal symmetry, as shown in the inset of Fig. 4c. The nonzero even components of SHG tensor are constrained by 31m symmetry, which means the independent elements are $\chi_{xx}^{\text{even}} (-= \chi_{zyy}^{\text{even}} = -\chi_{yxz}^{\text{even}})$, $\chi_{xzz}^{\text{even}} (= \chi_{yyz}^{\text{even}})$, $\chi_{zzx}^{\text{even}} (= \chi_{zyx}^{\text{even}})$ and $\chi_{zzz}^{\text{even}}$. The calculated SHG results are presented in Fig. 4d, which are consistent with the above symmetry analysis. Furthermore, the SHG effect is even with time-reversal symmetry, meaning that reversing the magnetic order does not lead to the reversion of SHG susceptibilities [Fig. 4d].

The G-wP type SHG effect originates from the magnetic structures, and it is even with time-reversal symmetry. These two characteristics are the distinctive features of the G-wP type SHG effect. The anomalous SHG effect in bulk VBr$_2$ refreshes the conventional understanding that magnetism can only contribute to the odd SHG tensors. In addition, the G-wP type SHG effect is not unusual in real materials, as 76 magnetic structures in the MAGDATA database are proposed to exhibit G-wP SHG effect (Fig. 3b). Therefore, the classification method is a powerful tool to explore exotic SHG phenomena in magnetically ordered materials.

If the magnetic moments of V atoms in the adjacent interlayers are parallel aligned, as exhibited in the inset of Fig. 4e, the MSG of this magnetic structure is $P31m'$. This magnetic structure leads to the BW-wP type SHG effect according to Fig. 2. The even and odd SHG tensors coexist, and both originate from magnetic structure. The even SHG susceptibilities are basically the same as those in Fig. 4d, and the odd parts are shown in Fig. 4e. We further investigate the SHG effect of bilayer VBr$_2$ with A-type AFM magnetism, as depicted in Fig. 4f. Due to PT symmetry, its bands are doubly degenerate, and the band energies of +k and −k points are not equivalent (as illustrated in the inset of Fig. 4g). Since its MSG is $P31m'$, the corresponding SHG effect belongs to the PT-wP type. Its SHG tensor has only the odd part, and the SHG tensor is constrained by the 32 (D$_3$) symmetry. The calculated SHG coefficients are shown in Fig. 4h, which are consistent with our symmetry analysis. Indeed, the SHG effect in bilayer VBr$_2$ with A-type AFM magnetism reverses with the magnetic order, similar to that of bilayer CrI$_3$ [25, 61].

**Example 2: SHG effect of RMnO$_3$ with various magnetic structures**

The parent phase of RMnO$_3$ (R = Sc, Y, In, Dy, Ho, Er, Tm, Yb and Lu) usually adopt the noncentrosymmetric structure with SG $P6_3cm$, as presented in Fig. 5a. The magnetism primarily arises from the Mn$^{3+}$, forming approximately equilateral triangles, as illustrated in the bottom panel of Fig. 5b. Below the Néel temperature, the strong super-exchange leads to 120° arrangement of the spins of Mn$^{3+}$ in the basal plane, and small displacements of Mn$^{3+}$ ions (occupy 6c positions, see Supplementary Table VIII) break the triangular frustration.

According to the MAGDATA database and Refs. [11, 16, 17, 62–65], RMnO$_3$ can exhibit various magnetic structures, such as $A_1$, $A_2$, $B_1$ and $B_2$ phase presented in Fig. 5b–e. For a specific hexagonal manganite, the ground magnetic order always belongs to one of these states, but can be manipulated among them under certain conditions. The pioneering works by Fiebig et al. [16, 17, 62–65] have proven the SHG effect is a powerful tool for investigating the magnetic structures of RMnO$_3$. In this section, we aim to further validate our theory and method with RMnO$_3$. This existing foundations enabled our current advances, and is instrumental in verifying the validity of our isomorphic theory and classification method.

The inversion symmetry breaking of the parent phases leads all RMnO$_3$ to exhibit SHG effects. The SHG effect of the $A_1$ phase belongs to the O-woP type, and the SHG effects of other three phases falls into the BW-woP type. The even SHG tensors of the four magnetic phases possess the same characteristics, which are constrained by PG $G_0 = 6mm$. However, the odd SHG tensors differ for every magnetic phase, due to the different symmetries constraints as shown in Fig. 5b–e. The calculated nonzero SHG susceptibilities of YMnO$_3$ with the four magnetic structures are depicted in Fig. 5b–e, which are consistent with the symmetry analysis results (see Supplementary Table X) and previous studies [11, 12, 16, 17, 62–65]. The magnitude of the even SHG susceptibilities are almost one order of magnitude larger than those of odd parts in RMnO$_3$, as presented in Fig. 5b, which may be caused by the weak spin-orbit coupling (SOC) effect [24–26] in YMnO$_3$.

The in-plane even SHG components $\chi_{abc}^{\text{even}}(a, b, c \in \{x, y\})$ vanish in all magnetic phases due to the $C_{2z}$ symmetry in $G_0 = 6mm$. However, the isomorphic groups $G_1$ of the $B_1$ and $B_2$ phases break the $C_{2z}$ symmetry, leading
In magnetically ordered materials, the SHG susceptibility can be expressed as a Tailor series expression in terms of the magnetic order parameter $M$ [11] (such as magnetic moment in a ferromagnet, the Néel vector in a collinear antiferromagnet and the chirality in a non-collinear antiferromagnet):

$$\chi_{ijk}^{(2)}(M^0) + \chi_{ijk}^{(2)}(M^1) + \chi_{ijk}^{(2)}(M^2) + \cdots,$$

where $\chi_{ijk}^{(2)}(M^0)$ is independent on magnetic order, corresponding to the SHG effect only contributed by crystallographic asymmetry. The odd-order Tailor expansion terms, including $\chi_{ijk}^{(2)}(M^1), \chi_{ijk}^{(2)}(M^3), \chi_{ijk}^{(2)}(M^5), \cdots$ contribute to the odd SHG tensors ($c$-type). As stated in Ref. [12], the even-type SHG effect ($i$-type) refer to non-invariance under spin reversal, allowing the even-order magnetic coupling ($\chi_{ijk}^{(2)}(M^2), \chi_{ijk}^{(2)}(M^4), \chi_{ijk}^{(2)}(M^6), \cdots$) to contribute SHG effect. In the PT-wP type SHG effect, such as bilayer CrI$_3$ [25, 61], the lowest Tailor term is $\chi(M^1)$, and only the odd-order terms exist. While for the G-wP type SHG effect, such as bulk VBr$_3$, the lowest Tailor term is $\chi(M^2)$, however the zero-order $\chi(M^0)$ and the linear-order term $\chi(M^1)$ are forbidden by symmetry.

It is noted that our study is mainly focused on the SHG effect induced by the bulk electric dipole. The classification method can also be extended to the SHG effect arising from surface electric dipole provided that the surface crystal and magnetic structures are given. In centrosymmetric materials, the magnetic-dipole-type and electric-quadrupole-type SHG are permitted by symmetry. For example, the SHG effect in Cr$_2$O$_3$ [68] and monolayer CrSBr [9]. Even thorough, there are prior works on magnetic-dipole SHG effect by Hanamura and Valentí et al. [51, 52, 69–71] using semi-classical methods to treat the magnetic-dipole moment operator, evaluating the magnetic-dipole-type and electric-quadrupole-type SHG effect in first-principles calculations remain tough issues. Because it is very complicated to accurately treat the magnetic-dipole and electric-quadrupole operators, and capture their interplay with electric fields in density functional theory (DFT). Hence, the magnetic-dipole-type and electric-quadrupole-type SHG effects are not numerically studied in this work. However, we think our isomorphic group method can also be applied to investigate the characteristics of these two SHG effects, which needs to be further studied.

According to the classification presented in Table II, the physical mechanisms of SHG effect can be classified...
into three main aspects: the even SHG effect arising from crystal asymmetry, even SHG effect caused by magnetic structure and odd SHG effect caused by magnetic structure. As summarized in Table III, we will compare them in the following. Specifically, the magnetic structure can contribute to both the odd and even SHG tensors, which vanish when the magnetic order or SOC effect in the coplanar magnetically ordered materials disappear. In this case, only the even SHG tensors contributed by the crystal structure asymmetry survive. For semiconducting magnetically ordered materials, $\chi^{\text{even}}$ is nonzero, while $\chi^{\text{odd}}$ disappears in the zero frequency limit ($\omega \to 0$).

The conditions to obverse them individually are in nonmagnetically ordered materials, G-wP type and PT-wP type magnetically ordered materials, respectively, as listed in Table III. The three parts in Table III can coexist in magnetically ordered materials whose parent phases have no inversion symmetry, corresponding to BW-wP and O-wP types SHG effect. It should be noted that the seven types of SHG identified in our work are required further experimental verification. Therefore, we encourage researchers to perform experiments and simulations to validate our proposed classification and uncover distinctive SHG characteristics in magnetically ordered materials.

In conclusion, the classification of SHG effect in magnetically ordered materials is performed to reveal the symmetries and physical mechanisms. Specifically, the isomorphic group method is utilized to study the SHG tensor for every MPG. This method simplifies the SHG tensor characteristics under MPGs into nonmagnetic PGs, revealing the symmetry rules governing SHG effect. Furthermore, a tensor dictionary containing SHG and LMO effects is created, serving as a guidance for experimentally probing magnetic structures. Subsequently, SHG effect is classified into seven distinct types based on the symmetries of the magnetic and parent crystal structures. Assisted by this classification, a database cataloging SHG and LMO effects of materials in MANG-DATA is established. The proposed classification method builds a close relationship between the SHG effect and magnetic structures, and enhance the understanding of the SHG effect in magnetically ordered materials.

**METHODS**

First-principles calculations

The first-principles calculations based on DFT are performed using the VASP software package [72, 73]. Moreover, the general gradient approximation (GGA) according to the Perdew-Burke-Ernzerhof (PBE) functional is employed, and the spin-orbit coupling effects are considered for all the materials. $U_{\text{eff}}=3.0$ eV (5.0 eV) is set for V (Mn) atoms in VBr$_2$ (YMnO$_3$) calculations. The Bloch wave functions are iteratively transformed into maximally localized Wannier functions using the Wannier90 package [74, 75]. The SHG susceptibilities and antisymmetric photoconductivities are calculated using our program WNLOP (Wannier Non-Linear Optics Package) based on the effective tight-binding (TB) Hamiltonian obtained by Wannier90.

**Symmetries analysis of magnetically ordered materials**

The symmetries of magnetically ordered materials are determined by the FINDSYM website [76], the and MPGs and MSGs are analyzed with the help of Bilbao Crystallographic Server [77]. The magnetic structures are visualized using VESTA software [78].

**DATA AVAILABILITY**

All data required to support the conclusions are presented in the paper. Additional data related to this paper can be requested from the authors.

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TABLE III. Distinctive features of different physical mechanisms of SHG effect in magnetically ordered materials.

| Condition                        | Even from crystal asymmetry | Even from magnetic structure | Odd from magnetic structure |
|----------------------------------|-----------------------------|-----------------------------|----------------------------|
| Without magnetic order           | ✓                           | ×                           | ×                          |
| Without SOC effect$^{(1)}$       | ✓                           | ×                           | ×                          |
| Zero frequency limit$^{(2)}$     | ✓                           | ✓                           | ×                          |
| Reverse magnetic order           | Invariant                   | Invariant                   | Reverse                    |
| Individually existing condition$^{(3)}$ | Nonmagnetically ordered materials | G-wP                      | PT-wP                      |

$^{(1)}$ For the coplanar magnetically ordered materials, see Supplementary Note 5.4 for more information.
$^{(2)}$ For semiconducting magnetically ordered materials, see Supplementary Note 5.5 for more information.
$^{(3)}$ “Individually existing condition” refers to the symmetry requirements to observe the SHG effect arising from crystal asymmetry, even SHG effect caused by magnetic structure and odd SHG effect caused by magnetic structure, individually.

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Author contributions
R.-C.X. conceived the project with H.L. and H. J.. R.-C.X. edited the code and performed the symmetry analysis and first-principles calculations. R.-C.X., H.J., and H.L. discussed the results and the writing. The manuscript was written through the contributions of all authors. All authors have approved the final version of the manuscript.

Competing interests
The authors declare that they have no competing financial or non-financial interests.

Additional information
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