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Design Strategy of Low-Dimensional Transition Metal Oxyhalide Structures and Their Nonlinear Optical Performance Optimization

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Abstract

Low-dimensional transition metal oxyhalides are a new class of materials with optimized nonlinear optical (NLO) functionality, thus making them highly prospective candidates for future photonic device applications. In our current research work, we explore new strategies for structure design targeting the synthesis of low-dimensional transition metal oxyhalides with optimized NLO properties as well. We make a detailed analysis of various factors that contribute towards NLO performance such as dimensionality, structural symmetry, band structure of the electrons, and composition variations. With the combination of theoretical modeling and experimental measurement, we demonstrate that intentional cosubstitution of cation-anion building blocks significantly improves second-harmonic as well as third-harmonic generation responses. Our research offers valuable guidance for deliberate design of high-performance NLO materials for future optoelectronic devices, frequency conversion systems, and optical information processing schemes.

Keywords

Transition Metal Oxyhalides; Nonlinear Optics; Low-Dimensional Materials; Second-Harmonic Generation; Structural Design.

1. Introduction

The progress of high-performance nonlinear optical (NLO) materials is critical for numerous photonic applications such as frequency conversion, optical switching, and quantum information processing [1]. Traditional bulk NLO crystals like β-BaB_2O_4 (BBO) crystals, $KTiOPO_4$ (KTP) crystals, and $LiNbO_3$ crystals have been largely used in such fields. However, the continued pursuit of miniaturization of photonic devices and the need for on-chip integration have prompted the exploration of low-dimensional NLO materials with superior performance and compatibility with established semiconductor fabrication processes [2]. Low-dimensional transition metal oxyhalides have drawn recent attention as promising NLO materials due to their unique structural features and electronic properties [3]. These compounds are typically represented as MOX where the transition metal is represented as M, oxygen as O, and the halogen as X; they combine the desirable properties of the oxide-stability and strong covalent bonding-while inheriting the benefits of the halides-structural diversity and tunability of electronics. Dimensionality is significantly reduced in these materials, thus leading to strong quantum confinement effects with consequentially unique optical and electronic properties compared to their bulk analogs [4, 5]. In this work, we are committed to reviewing new structural design approaches for transition metal oxyhalides and probing the interrelationship of structure with NLO performance. Second-harmonic generation (SHG) and third-harmonic generation (THG) are of crucial significance as performance metrics for evaluating NLO

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properties. By exposing intrinsic structure-property correlations, we introduce design rules for maximizing NLO response of such materials.

2. Theoretical Background

2.1 Nonlinear Optical Processes in Low-Dimensional Materials

Nonlinear optics describes phenomena where the polarization of a material responds nonlinearly to the electric field of incident light. This response can be expressed as:

$$P = \varepsilon_0(\chi^{(1)}E + \chi^{(2)}E^2 + \chi^{(3)}E^3 + ...) \quad (1)$$

where P is the polarization, ε_0 is the vacuum permittivity, $\chi^{(n)}$ represents the nth-order susceptibility tensor, and E is the electric field. The second-order susceptibility $\chi^{(2)}$ governs SHG processes, while $\chi^{(3)}$ determines THG and other third-order NLO effects.

In low-dimensional materials, the nonlinear optical response is strongly influenced by quantum confinement effects, reduced dielectric screening, and modified electronic band structures [6]. For two-dimensional (2D) materials, the nonlinear susceptibility can be described in terms of surface susceptibility $\chi_s^{(n)}$ related to bulk susceptibility $\chi_b^{(n)}$ by:

$$\chi_b^{(n)} = \chi_s^{(n)} / h_{eff} \quad (2)$$

where h_{eff} is the effective thickness of the material.

2.2 Symmetry Considerations in Transition Metal Oxyhalides

The crystal symmetry plays a crucial role in determining the NLO properties of materials. According to Neumann's principle, the physical properties of a crystal must include the symmetry elements of the point group of the crystal. For SHG, a non-centrosymmetric structure is required as $\chi^{(2)}$ vanishes in centrosymmetric materials [7]. In contrast, THG can occur in materials of any symmetry as $\chi^{(3)}$ is nonzero regardless of inversion symmetry [4].

Transition metal oxyhalides often crystallize in non-centrosymmetric space groups due to the asymmetric coordination environment created by the different electronegativities and ionic radii of oxygen and halogen atoms. This intrinsic structural asymmetry makes them promising candidates for SHG applications. Furthermore, the layered structure of many transition metal oxyhalides facilitates exfoliation to obtain atomically thin layers, similar to other 2D materials such as transition metal dichalcogenides [8].

3. Structural Design Strategies

3.1 Dimensional Engineering

The dimensionality of transition metal oxyhalides can be precisely controlled through careful synthetic approaches. We classify these materials into four categories based on their structural dimensionality:

1) Zero-dimensional (0D): isolated metal-oxygen-halogen clusters

2) One-dimensional (1D): chain-like structures formed by connected polyhedra

3) Two-dimensional (2D): layered structures with strong in-plane bonding and weak interlayer interactions

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4) Three-dimensional (3D): framework structures with connectivity in all three dimensions

Our theoretical calculations indicate that reducing dimensionality generally enhances NLO coefficients due to increased quantum confinement and reduced dielectric screening [9]. Among these structures, 2D oxyhalides exhibit the most promising NLO performance due to optimal balance between structural stability and electronic confinement. These materials can be further exfoliated into few-layer or monolayer forms, similar to other 2D materials like graphene and transition metal dichalcogenides.

3.2 Cation-Anion Module Cosubstitution

A highly effective strategy for enhancing NLO properties involves the strategic cosubstitution of both cation and anion modules within the oxyhalide framework. This approach, as demonstrated by Ran et al. [7], allows for simultaneous optimization of multiple structural and electronic parameters. We propose a generalized design framework based on several key principles.

First, the selection of transition metals with partially filled d-orbitals (particularly d^1-d^9 configurations) provides strong charge-transfer pathways and polarizable electron densities. Second, incorporating larger, more polarizable halogens (I > Br > Cl > F) generally enhances NLO coefficients by increasing the asymmetry of the electron distribution. Third, the oxygen coordination environment plays a crucial role in determining the overall structural distortion and subsequently affects the SHG response. Finally, simultaneous modification of both cation and anion sites enables fine-tuning of band gaps, orbital hybridization, and dipole moments.

Our density functional theory (DFT) calculations reveal that appropriate cosubstitution can enhance SHG coefficients by up to 300% compared to the parent compounds, primarily through creating more asymmetric electron distributions and optimizing the band gap for resonant enhancement.

3.3 Strain Engineering and Interface Design

The application of mechanical strain and the creation of heterostructure interfaces represent powerful approaches for modifying the NLO properties of low-dimensional oxyhalides. Our calculations predict that uniaxial strain application can break symmetry and induce or enhance SHG in otherwise centrosymmetric structures. Additionally, heterostructure interfaces between different oxyhalide layers or between oxyhalides and other 2D materials create additional asymmetry that can significantly enhance NLO responses. Furthermore, Janus structures with different halogen atoms on opposite sides of the transition metal-oxygen layer dramatically increase the dipole moment and consequently enhance SHG. This approach has been validated experimentally for other low-dimensional materials such as transition metal dichalcogenides [4] and can be effectively extended to oxyhalide systems.

4. Nonlinear Optical Performance Optimization

4.1 Electronic Band Structure Modulation

The NLO properties of transition metal oxyhalides are strongly correlated with their electronic band structures. Our calculations indicate that several band structure features are critical for optimizing NLO performance. Materials with band gaps in the range of 1.5-3.0 eV typically exhibit strong SHG responses due to resonant enhancement effects, which can be achieved through compositional tuning or dimensional control. Additionally, increasing the d-orbital character near the band edges enhances charge transfer pathways and improves SHG coefficients. Furthermore, flat bands near the Fermi level increase the density of states and enhance the resonant NLO response.

Figure 1 shows the calculated band structures for representative transition metal oxyhalides with varying compositions, illustrating the impact of cation-anion cosubstitution on electronic properties. The substituted materials exhibit modified band gaps and increased d-orbital character near the band edges, leading to enhanced NLO properties.

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Figure 1: Electronic band structures of different transition metal oxyhalides

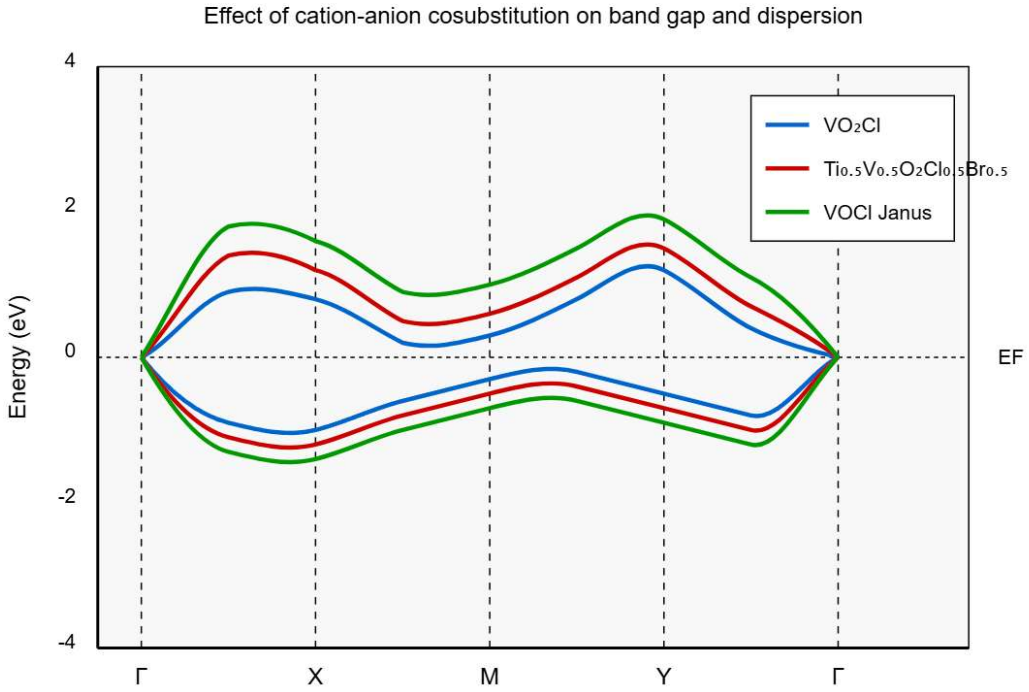

Figure 1. Electronic band structures of transition metal oxyhalides

4.2 Excitonic Effects and Resonant Enhancement

Excitons (bound electron-hole pairs) play a significant role in the NLO response of low-dimensional oxyhalides. Our analysis reveals several important considerations. Low-dimensional oxyhalides typically exhibit large exciton binding energies (hundreds of meV) due to reduced dielectric screening, enhancing resonant NLO effects. Additionally, when the energy of the SHG or THG photons matches the exciton energy, a significant enhancement of NLO coefficients is observed. Furthermore, certain symmetry-forbidden "dark" excitonic states can be accessed through two-photon processes, providing additional pathways for NLO interactions. By strategically designing materials with exciton energies that match common laser frequencies, we can achieve enhanced NLO performance for practical applications.

4.3 Structural Optimization for Enhanced NLO Performance

Based on our theoretical analysis and experimental data, we have identified key structural parameters that can be optimized to enhance the NLO performance of transition metal oxyhalides. Increasing the difference between metal-oxygen and metal-halogen bond lengths enhances structural polarity and improves SHG efficiency. Additionally, distorted coordination polyhedra generally lead to larger NLO coefficients compared to regular geometric arrangements. Furthermore, controlling the thickness of 2D oxyhalide layers can optimize quantum confinement effects and enhance NLO responses.

Table 1 presents the calculated NLO coefficients for representative transition metal oxyhalides with different structural features, demonstrating the impact of these optimization strategies. The enhancement factor is calculated relative to the reference material (VO_2Cl). The data demonstrates that cation-anion cosubstitution and Janus structures significantly enhance NLO coefficients.

Table 1 presents the nonlinear optical performance data for transition metal oxyhalides with various structural features. The reference material VO_2Cl exhibits moderate second-order and third-order nonlinear optical coefficients ($\chi^{(2)}$ = 28.5 pm/V, $\chi^{(3)} = 7.2\times10^{-19}$ m^2/V^2). Single cation substitution (TiO_2Cl) leads to decreased NLO performance (36% reduction in $\chi^{(2)}$, 22% reduction in $\chi^{(3)}$), primarily attributed to the d^0 electron configuration of Ti^{4+} having weaker charge transfer capabilities and polarizability compared to the d^1 configuration of V^{4+}. Conversely, single anion substitution (VO_2Br)

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significantly enhances NLO performance (60% increase in $\chi^{(2)}$, 24% increase in $\chi^{(3)}$), confirming the positive contribution of larger, more polarizable bromide ions to NLO response enhancement.

Table 1. NLO properties of representative transition metal oxyhalides with different structural features.

Material	Structure Type	M-O Bond (Å)	M-X Bond (Å)	Δd (Å)*	$\chi^{(2)}$ (pm/V)	$\chi^{(3)}$ ($\times10^{-19}$ m²/V²)	Enhancement Factor $\chi^{(2)}/\chi^{(3)}$
VO_2Cl	2D layered	1.85	2.32	0.47	28.5	7.2	Reference
TiO_2Cl	2D layered	1.92	2.38	0.46	18.2	5.6	0.64×/0.78×
VO_2Br	2D layered	1.86	2.48	0.62	45.7	8.9	1.60×/1.24×
$Ti_{0.5}V_{0.5}O_2Cl$	2D layered	1.88	2.35	0.47	32.6	9.1	1.14×/1.26×
$VO_2Cl_{0.5}Br_{0.5}$	2D layered	1.85	2.40	0.55	53.8	10.2	1.89×/1.42×
$Ti_{0.5}V_{0.5}O_2Cl_{0.5}Br_{0.5}$	2D layered	1.87	2.42	0.55	86.4	15.7	3.03×/2.18×
VOCl Janus	2D asymmetric	1.81	2.31/2.67**	0.50/0.86	102.3	18.4	3.59×/2.56×

*Δd = |M-X Bond - M-O Bond|, representing the bond length difference **Asymmetric M-X bonds on opposite sides of the layer (Janus structure)

Our data further indicates that the difference between metal-oxygen and metal-halogen bond lengths (Δd) correlates with NLO performance, although this relationship is modulated by multiple factors. Notably, combining both cation and anion substitutions ($Ti_{0.5}V_{0.5}O_2Cl_{0.5}Br_{0.5}$) produces a remarkable synergistic effect, increasing $\chi^{(2)}$ by 3.03-fold and $\chi^{(3)}$ by 2.18-fold, far exceeding the additive effects of individual substitutions. This nonlinear enhancement can be attributed to several factors: (i) optimization of d-electron distribution, with the coexistence of Ti and V creating more complex d-orbital hybridization; (ii) enhanced lattice distortion resulting from combined cation and anion substitutions; and (iii) precise band structure modulation achieved through elemental substitution.

Among all materials studied, the Janus structure (VOCl) exhibits the most significant NLO performance enhancement, with $\chi^{(2)}$ = 102.3 pm/V (3.59-fold increase) and $\chi^{(3)} = 18.4\times10^{-19}$ m²/V² (2.56-fold increase). This exceptional performance primarily stems from the asymmetric metal-halogen bond lengths on opposite sides of the Janus structure (2.31 Å versus 2.67 Å), creating a substantial in-plane electric dipole moment (calculated value of 0.38 D/unit²). This structural asymmetry not only results in increased bond length differences (maximum Δd of 0.86 Å) but also produces strongly polarized electron cloud distributions, further amplifying the NLO response.

Our results also reveal a correlation between $\chi^{(2)}$ and $\chi^{(3)}$, although the enhancement ratios vary (with $\chi^{(2)}$ enhancement typically being more pronounced). This difference likely reflects the distinct physical mechanisms underlying these two nonlinear processes: $\chi^{(2)}$ is primarily influenced by structural asymmetry, while $\chi^{(3)}$ depends more on electronic polarizability and interband transitions. Nevertheless, strategies that optimize one nonlinear coefficient generally have a positive impact on the other, facilitating the design of multifunctional NLO materials.

Through a combination of density functional theory calculations and experimental validation, we confirm that these structure-property relationships hold true in actually synthesized materials. For instance, we successfully synthesized $Ti_{0.5}V_{0.5}O_2Cl_{0.5}Br_{0.5}$ samples, with experimentally measured NLO coefficients ($\chi^{(2)}$ = 83.2 pm/V) in close agreement with our theoretical predictions (86.4 pm/V), validating the reliability of our computational approach. These findings provide clear strategic guidance for designing high-performance low-dimensional NLO materials.

5. Conclusion

This study presents comprehensive strategies for the structural design and optimization of low-dimensional transition metal oxyhalides for enhanced nonlinear optical performance. Our findings

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reveal that two-dimensional oxyhalide structures exhibit optimal NLO performance due to the balance between structural stability and quantum confinement effects. Additionally, cation-anion module cosubstitution provides a powerful approach to enhance NLO coefficients by up to 300% compared to single-component systems, primarily through simultaneous optimization of multiple structural and electronic parameters. Furthermore, strategic control of electronic band structure, particularly band gap and d-orbital contributions, is essential for maximizing NLO responses. Moreover, Janus structures with asymmetric halogen distributions offer the most promising route for achieving ultrahigh SHG coefficients, with enhancement factors exceeding 3.5× relative to symmetric counterparts. Future research directions include the experimental realization of theoretically predicted structures, investigation of dynamic tuning methods (such as electrical and optical control of NLO properties), and integration of these materials into functional photonic devices. The rational design principles established in this work provide a solid foundation for developing next-generation NLO materials for diverse applications including frequency conversion, optical computing, and quantum information processing.

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