Metal oxyhalides: an emerging family of nonlinear optical materials

Xinglong Chen* and Kang Min Ok*

Second-order nonlinear optical (NLO) materials have drawn enormous academic and technological attention attributable to their indispensable role in laser frequency conversion and other greatly facilitated applications. The exploration of new NLO materials with high performances thus has long been an intriguing research field for chemists and material scientists. However, an ideal NLO material should simultaneously satisfy quite a few fundamental yet rigorous criteria including a noncentrosymmetric structure, large NLO coefficients, desired transparent range, large birefringence, high laser damage threshold, and availability of a large-size single crystal. Therefore, the identification of promising compound systems, targeted design, and experience-based syntheses are crucial to discover novel NLO materials working in the spectral region of interest. As an important family of mixed-anion compounds, versatile metal oxyhalides containing metal-centered oxyhalide functional units ([MO$_m$X$_n$] (X = F, Cl, Br, and I)) are becoming a marvelous branch for interesting NLO materials. Especially, when the central metals are d$^0$/d$^{10}$ transition metals or heavy post-transition metals, a number of novel NLO materials with superior functionalities are expected. Our thorough review on the recent achievements of metal oxyhalides for NLO materials are divided into the fast-growing NLO metal oxyhalides with single type halogen anions and the newly identified NLO metal oxyhalides with mixed halogen anions. Here we mainly focus on the design strategy, structural chemistry, NLO-related properties, and structure–property correlation of the metal oxyhalides with relatively large NLO responses. We hope this review can provide an insight on the rational design and future development of emerging metal oxyhalides for NLO and other applications.

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1. Introduction

The second-order nonlinear optical (NLO) phenomenon, i.e., second-harmonic generation (SHG) characterized by the frequency-doubling effect, was first observed by Franken and coworkers during the laser applying experiment on a non-centric symmetric (NCS) quartz soon after the invention of the laser, an unprecedented coherent light source with single-frequency and ultra-high irradiance. Since then, a variety of NLO materials that can constructively expand the wavelengths of lasers have been greatly promoting the development of laser science and other numerous scientific and technological fields. Therefore, the development of superior performing NLO materials has been attracting immense interest. A few widely used NLO crystals include AgGaS₂ (AGS), AgGaSe₂ (AGSe), ZnGeP₂ (ZGP), KTiOPo₄ (KTP), LiNbO₃ (LN), KH₂PO₄ (KDP), β-βaBa₅O₄ (BBO), LiB₅O₄ (LBO), CsLiB₅O₁₀ (CLBO), KBe₂BO₆F₂ (KBBF). Among them, only the “oxygen-free” crystals such as AGS, AGSe, and ZGP are applicable to the mid-infrared (mid-IR) spectral region (3–20 μm) owing to their superior IR transparent range (<12 μm) and robust NLO effects. Unfortunately, however, their applications have been fiercely restricted by some intrinsic flaws such as an inadequate laser damage threshold (LDT) for AGS, harmful two photon absorption for ZGP, and non-phase-matching behavior for AGSe. Meanwhile, KBBF has been considered to be a very good NLO material working in the deep-ultraviolet (deep-UV) region (<200 nm). However, growing large crystals of KBBF is very difficult to obtain a superb NLO material with balanced overall performance. It should be noted that the requirements are inversely correlated. For criterion (4), as materials with large band gaps tend more likely to prevent the laser-induced damage, NLO crystals with large band gaps are normally pursued, which is consistent with criterion (1) where large band gaps are needed to ensure a wide transparent range in the UV side of the transparent windows, although the definition of “large” varies considerably depending on the practical working wavelengths of NLO materials (see below). Moreover, some of the parameters in the above-mentioned requirements are inversely correlated. For example, the inverse relationship between the band gap and SHG response makes it more difficult to obtain a superb NLO material with balanced overall performance. It should be noted that the more detailed requirements for SHG response, LDT, and band gap vary for the NLO materials according to their working spectral regions and other specific purposes. For instance, an ideal mid-IR NLO material is preferred to have a larger band gap (>2.62 eV) than those of the commercial NLO materials (e.g., AGS, AGSe, ZGP), a larger LDT than that of AGS (30 MW cm⁻²), a comparable NLO response to that of AGS [at least 20.5 × AGS (13 pm V⁻¹)], and wide IR transparency (usually >5 μm, ideally >10 μm). An ideal Vis-NIR NLO material should have a strong SHG response comparable to that of KTP [20.5 × KTP (3.7 pm V⁻¹)] and a band gap larger than that of KTP (>3.54 eV). For an ideal DUV NLO material, a much wider band gap (>6.2 eV) and an SHG response larger than that of KDP (0.39 pm V⁻¹) are required.

In this context, numerous efforts have been made to design and synthesize new inorganic NLO materials, which include the exploration of metal chalcogenides and metal halides for mid-IR NLO materials, various oxide-based metal salts for UV and Vis-NIR NLO materials, and fluorooxoborates and fluoro phosphates for deep-UV NLO materials. Notably, the study of mixed-anion compounds such as metal oxysulfides, metal chalcogenide halides, and metal oxysulfides has shown light on the development of many NLO materials. Among them, the
emerging NLO metal oxyhalides have recently received growing interest. Broadly speaking, metal oxyhalides refer to all compounds containing metal-centered oxyhalide groups, \([\text{MO}_n\text{X}_n](X = F, Cl, Br, and I)\). Especially, the \([\text{MO}_n\text{X}_n]\) units act as important functional building blocks (FBBs), although the metal oxyhalides with additional anionic groups (e.g., \([\text{BO}_3]\)) are usually identified as metal salt halides. In the \([\text{MO}_n\text{X}_n]\) group, the metal cation is coordinated by at least two types of multiple anions such as \(O^{2-}\) and \(X^-\) rather than a single type of anion. Materials containing central metals of \([\text{MO}_n\text{X}_n]\) belonging to the \(d^0/d^{10}\) transition metals or heavy post-transition metals manifesting second-order Jahn–Teller (SOJT) distortions are of particular interest.27 The SOJT distortions of \([\text{MO}_n\text{X}_n]\) groups can induce large local asymmetry, which would be superimposed to large macroscopic asymmetry when the \([\text{MO}_n\text{X}_n]\) groups are well-aligned. Therefore, the formed metal–oxyhalide polyhedra can be preferable FBBs for the design and discovery of novel NLO materials, owing to their asymmetric characteristics that have natural advantages in producing NCS structures, strong SHG effects, as well as large optical anisotropies (birefringences). Consequently, there has been rising consciousness that metal oxyhalides can be a marvelous branch for the exploration of high-performance NLO materials.

Herein, we give a brief retrospect of the recently discovered metal oxyhalides that exhibit intriguing NLO properties. In this review, the metal oxyhalides are divided into two categories: the first category is the classic NLO metal oxyhalides that only contain single type halogen anions, including those with additional NLO-active anionic groups (e.g., \([\text{BO}_3]\), \([\text{BO}_4]\), \([\text{CH}_3\text{COO}\]), \([\text{NO}_3]\), \([\text{VO}_4]\), \([\text{SeO}_3]\), \([\text{IO}_3]\)) which are characterized by proved direct contributions to NLO responses of materials owing to their considerable local asymmetry, as well as the so-called “pure” metal oxyhalides without additional anionic groups. The other one is the newly emerged NLO metal oxyhalides with more than one type of halogen anions. Among the metal cations that form the oxyhalide polyhedra, only \(d^0/d^{10}\) transition metal cations (\(\text{Ti}^{4+}, \text{V}^{2+}, \text{Mo}^{6+}, \text{Zn}^{2+}, \text{Cd}^{2+}\), etc.) and post-transition metal cations (\(\text{Pb}^{2+}, \text{Bi}^{3+}, \text{Sn}^{2+}\), etc.) are included. In addition, we are mainly focusing on the cases in which the \([\text{MO}_n\text{X}_n]\) groups make considerable contributions to SHG responses. The examination contains material design strategies, structures, syntheses, structure-driven NLO-related properties, and structure–property correlation. We also make a broader comparison of the discussed NLO metal oxyhalides and provide a perspective on the future development of metal oxyhalide NLO materials.

2. NLO metal oxyhalides with single type halogen anions

2.1 NLO metal oxyhalides with additional anionic groups

2.1.1 NLO metal oxyhalide borates

\(\text{Pb}_2\text{BO}_3\text{X}(X = \text{Cl, Br, and I}).\) Crystallizing in the trigonal NCS space group, \(P3121\), the isostructural \(\text{Pb}_2\text{BO}_3\text{Cl}\), \(\text{Pb}_2\text{BO}_3\text{Br}\), and \(\text{Pb}_2\text{BO}_3\text{I}\) belong to the KBBF family. Although the structures of \(\text{Pb}_2\text{BO}_3\text{X}\) have been described as cationic \(\text{[Pb}_2\text{BO}_3\text{]}^+\) layers and interlayered \(\text{X}^-\) anions in the literature, here we would provide an alternative structural description for the materials in terms of metal–oxyhalides. The structures are constructed from \(\text{Pb}–\text{oxyhalide polyhedral groups, [PbO}_3\text{X}_2\), shared by well-arranged \([\text{BO}_3]\) trigonal planar units through oxygen atoms (Fig. 1). Single crystals of \(\text{Pb}_2\text{BO}_3\text{Cl}\) were grown from the melt of stoichiometric mixtures of \(\text{PbO}, \text{PbCl}_2, \text{and} \text{H}_2\text{BO}_3\), and \(\text{H}_2\text{O},\) possibly attributable to the decreased thermostability of \(\text{Pb}_2\text{BO}_3\text{Br}\) and \(\text{Pb}_2\text{BO}_3\text{I}\) caused by the volatility of the corresponding halide anions. \(\text{Pb}_2\text{BO}_3\text{Cl}\) melts congruently with a melting point of 630 °C, whereas \(\text{Pb}_2\text{BO}_3\text{Br}\) and \(\text{Pb}_2\text{BO}_3\text{I}\) decompose before melting. The SHG responses of \(\text{Pb}_2\text{BO}_3\text{Cl}, \text{Pb}_2\text{BO}_3\text{Br}, \text{and} \text{Pb}_2\text{BO}_3\text{I}\) are 9×, 9.5×, and 10× KDP, respectively, which are among the largest in the KBBF family. The remarkable SHG responses should be attributed to the synergistic effects of the \([\text{PbO}_3\text{X}_2]\) and coplanar arranged \([\text{BO}_3]\) NLO-active groups. It should be noticed that \(\text{Pb}_2\text{BO}_3\text{Cl}\) possesses many excellent properties for a promising NLO material in the Vis–NIR region, which include considerable SHG efficiency, sufficient birefringence (0.12@1064 nm), the largest band gap (3.99 eV) in the family, the highest thermostability, and facile growth of large crystals thanks to the congruently melting behavior.

\(\text{Pb}_2\text{B}_5\text{O}_9\text{X}(X = \text{Cl, Br, and I}).\) Isomorphic \(\text{Pb}_2\text{B}_5\text{O}_9\text{X}(X = \text{Cl, Br, and I}),\) crystallizing in the orthorhombic polar space group \(Pmn2_1\), belong to the derivatives of the hilgardite structure.31 Different from the isolated \([\text{BO}_3]\) group in \(\text{Pb}_2\text{BO}_3\text{X}\), \([\text{BO}_4]\) and \([\text{BO}_3]\) are polymerized to form a 3D open-framework of zeolitic \([\text{B}_5\text{O}_9]\_\text{X}^-\) in \(\text{Pb}_2\text{B}_5\text{O}_9\text{X}\) (Fig. 2). \(\text{Pb}^{2+}\) cations are coordinated by \(\text{O}^{2-}\) and \(\text{X}^-\) to form distorted \(\text{Pb}–\text{oxyhalide polyhedra, [PbO}_3\text{X}_2\), which are further connected to the \([\text{B}_5\text{O}_9]\_\text{X}^-\) framework by bridging \(\text{O}\) atoms. Remarkably, the \([\text{PbO}_3\text{I}_2]\) polyhedra in \(\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}\) exhibit significantly larger SOJT distortions than those of \([\text{PbO}_3\text{Cl}_2]\) and \([\text{PbO}_3\text{Br}_2]\) polyhedra in \(\text{Pb}_2\text{B}_5\text{O}_9\text{Cl}\) and
**NLO metal oxalate acetates**

Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ (X = Br and I) have been successfully synthesized by incorporating acetate groups into lead halide perovskites with the aid of a facile solvothermal method. Noticeably, large crystals up to 8 mm long with the needle-like growth habit could be easily grown. Isostructural Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ (X = Br and I), two new crystals of Rb$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ (X = Br and Cl) were successfully synthesized by solvothermal reactions. Although isostructural to Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$, Rb$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ exhibits a larger birefringence (0.18@1064 nm), a stronger SHG response (6.6 eV), and a relatively large band gap (3.12 eV), demonstrating that the replacement of alkali metal cations could improve the NLO properties. Meanwhile, for Rb$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$, the substitution of Cl$^-$ for Br$^-$ anions leads to a larger band gap (3.64 eV), the broader UV transmittance (down to 287 nm), and the higher LDT.

2.1.3 NLO metal oxalate nitrates

Bi$_3$O$_6$F$_2$(NO$_3$)$_3$ crystallizes in the polar NCS space group, R3. It features a double layered structure, which consists of asymmetric [BiO$_3$F$_2$] polyhedra, [NO$_3$]$^-$ trigonal planar groups, and isolated F$^-$ anions (Fig. 4). In the highly unsymmetrical [BiO$_3$F$_2$] polyhedra containing lone pairs, the Bi–O lengths are 2.13(3), 2.54, and 3.33 eV, respectively, following the usual band gap trend for halides. It is noteworthy that, a large single crystal of Pb$_2$O$_2$Cl, Pb$_2$O$_2$Br, and Pb$_2$O$_2$I are measured to be 3.72, 3.54, and 3.33 eV, respectively, following the usual band gap trend for halides. It is noteworthy that, a large single crystal of Pb$_2$O$_2$Cl (25 × 6 × 2 mm$^3$) has been successfully grown by a high temperature solution method using the PbCl$_2$–B$_2$O$_3$ flux system. In addition to the above compounds, the NLO properties of CsZn$_2$BO$_3$X$_2$ (X = F and Cl)$^{12}$ containing [ZnO$_3$X]$^-$ oxalate groups are also summarized in Table 1.

2.1.2 NLO metal oxalate acetates

Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ reveal remarkable phase-matching SHG responses of 4× and 8× KDP, respectively, as well as large birefringences of 0.15 and 0.26 at 1064 nm, respectively. Dipole moment calculations indicate that although the polarizations of [PbO$_2$X$_4$] polyhedra are opposite to those of [CH$_3$COO] groups along the polar c-axis, the net dipole moments in the unit cells are still large owing to the predominant contribution of [PbO$_2$X$_4$] groups. Therefore, the highly distorted [PbO$_2$X$_4$] polyhedra should be responsible for the strong SHG responses. Besides, the enhanced SHG of Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ compared to that of Cs$_3$Pb$_2$(CH$_3$COO)$_2$Br$_5$ can be explained by the corrected total dipole moment, which is inversely correlated with the volume and the square of band gaps. As is well known that the substitution of I for Br results in the decrease of the band gap, the experimental band gap of Cs$_3$Pb$_2$(CH$_3$COO)$_2$I$_5$ (2.55 eV) is smaller than that of Cs$_3$Pb$_2$(CH$_3$COO)$_2$Br$_5$ (3.26 eV).

**Fig. 2** Crystal structure of Pb$_2$B$_5$O$_9$Br viewed along the c-axis.
Table 1: Space groups, metal-oxyhalide unit types, and key properties of NLO metal oxyhalides with single type halogen anions

<table>
<thead>
<tr>
<th>No.</th>
<th>Crystal</th>
<th>Metal-oxyhalide unit type</th>
<th>SHG&lt;sup&gt;a&lt;/sup&gt;</th>
<th>IR-cutoff edge&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Birefringence&lt;sup&gt;c&lt;/sup&gt; (calculated)</th>
<th>LD&lt;sup&gt;d&lt;/sup&gt; (MW cm&lt;sup&gt;−2&lt;/sup&gt;)</th>
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<tr>
<td>1</td>
<td>PbO&lt;sub&gt;2&lt;/sub&gt;Cl&lt;sub&gt;2&lt;/sub&gt; (ref. 28)</td>
<td>9 × KDP</td>
<td>3.39</td>
<td>0.11@1064 nm</td>
<td>0.035@1064 nm</td>
<td>6.68&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>2</td>
<td>PbO&lt;sub&gt;2&lt;/sub&gt;Br&lt;sub&gt;2&lt;/sub&gt; (ref. 29)</td>
<td>6 × KDP</td>
<td>3.84</td>
<td>0.25@1064 nm</td>
<td>0.18@1064 nm</td>
<td>6.0&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>PbO&lt;sub&gt;2&lt;/sub&gt;I&lt;sub&gt;2&lt;/sub&gt; (ref. 30)</td>
<td>5.0 × KDP</td>
<td>4.0</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td>4</td>
<td>CsZn&lt;sub&gt;2&lt;/sub&gt;BO&lt;sub&gt;3&lt;/sub&gt;F&lt;sub&gt;2&lt;/sub&gt; (ref. 31)</td>
<td>6 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>5</td>
<td>Cs&lt;sub&gt;3&lt;/sub&gt;Pb&lt;sub&gt;2&lt;/sub&gt;(CH&lt;sub&gt;3&lt;/sub&gt;COO)&lt;sub&gt;2&lt;/sub&gt;I&lt;sub&gt;5&lt;/sub&gt; (ref. 32)</td>
<td>6 × KDP</td>
<td>3.84</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>6</td>
<td>BaBi(S&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;Cl) (ref. 33)</td>
<td>5 × KDP</td>
<td>3.48</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>7</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Cl (ref. 34)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>8</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 35)</td>
<td>5 × KDP</td>
<td>3.84</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>9</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 36)</td>
<td>5 × KDP</td>
<td>3.84</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 37)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<td>11</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 38)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td>12</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 39)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>13</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 40)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<tr>
<td>14</td>
<td>BaBi(SeO&lt;sub&gt;3&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;Br (ref. 41)</td>
<td>5 × KDP</td>
<td>3.77</td>
<td>0.279@1064 nm</td>
<td>0.279@1064 nm</td>
<td>0.27&lt;sup&gt;e&lt;/sup&gt;</td>
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<sup>a</sup> The SHG intensity was measured at 1064 nm when using KDP as the reference and at at ~2.1 μm when using KTP or AOS as the reference.<br><sup>b</sup> The IR cutoff edge was preliminarily measured on powder samples. The IR cutoff edge was estimated on single crystals. The LDT was measured on powder samples rather than single crystals.<br><sup>c</sup> The LDT was measured on powder samples. The LDT was measured on single crystals. The LDT was estimated on single crystals.
group, $Cm$, and the structure is composed of corner-sharing $[\text{CdO}_2\text{Cl}_4]$ groups and $[\text{VO}_4]$ groups (Fig. 5). The $\text{Cd}^{2+}$ cation in the $[\text{CdO}_2\text{Cl}_4]$ octahedron with a highly asymmetric coordination environment is bonded by four Cl/O and two O/O with the Cd–Cl and Cd–O distances of 2.584(3)–2.859(4) Å and 2.195(6) Å, respectively. Consequently, $\text{Cs}_2\text{CdV}_2\text{O}_6\text{Cl}_2$ has a large phase-matchable SHG response of approximately 5 times that of KDP. In addition, properties of another recently reported NLO cadmium oxybromide vanadate, $\text{Cs}_3\text{CdV}_4\text{O}_{12}\text{Br}_{16}$ containing the distorted $[\text{CdO}_2\text{Br}_2]$ groups are also summarized in Table 1.

### 2.1.5 NLO metal oxyhalide selenites/tellurites

$\text{BaBi(SeO}_3\text{)}_2\text{Cl}$. The barium bismuth oxychloride selenite, $\text{BaBi(SeO}_3\text{)}_2\text{Cl}$ with the orthorhombic polar structure (space group: $Cmc2_1$) was synthesized through a hydrothermal reaction at a mild temperature of 200 °C. The structure of $\text{BaBi(SeO}_3\text{)}_2\text{Cl}$ consists of 2D $[\text{Bi(SeO}_3\text{)}_2\text{Cl}]^{2-}$ anionic layers stacking along the [010] direction, and the charge-balancing $\text{Ba}^{2+}$ cations are intercalated between the neighboring layers.

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**Fig. 3** Crystal structure of $\text{Cs}_3\text{Pb}_2(\text{CH}_3\text{COO})_2\text{I}_5$ viewed along the $a$-axis ($\text{Cs}$–O and $\text{Cs}$–I bonds have been omitted for clarity).

**Fig. 4** Crystal structure of $\text{Bi}_6\text{O}_6\text{F}_5(\text{NO}_3)$ viewed along the $b$-axis.

**Fig. 5** Crystal structure of $\text{Cs}_2\text{CdV}_2\text{O}_6\text{Cl}_2$ viewed along the $c$-axis ($\text{Cs}$–O and $\text{Cs}$–Cl bonds have been omitted for clarity).

**Fig. 6** Crystal structure of $\text{BaBi(SeO}_3\text{)}_2\text{Cl}$ viewed along the $a$-axis ($\text{Ba}$–O and $\text{Ba}$–Cl bonds have been omitted for clarity).
(Fig. 6). Each [Bi(SeO₃)₂Cl]²⁻ layer is comprised of Bi–oxychloride groups, [BiO₂Cl], and [SeO₃] trigonal pyramids that are bridging through oxygen atoms. Notably, the acentric [BiO₂Cl] groups are aligned roughly toward the [001] direction by Cl⁻ ions, which is believed to generate the large macroscopic dipole moment of the compound. Excitingly, the material displays an exceptionally strong powder SHG response (16× KDP) with a phase-matching behavior at 1064 nm. In addition, the material is thermally stable up to 300 °C, has a band gap of 3.4 eV, and has a sufficient birefringence of 0.1 for phase-matching in a wide spectral range.

BiFSeO₃. BiFSeO₃ (ref. 38) was obtained by an aliovalent substitution approach using the polar model material, BiOIO₃ (ref. 39) with a very large SHG response (12.5× KDP). The substitution of [SeO₃]²⁻ groups for [IO₃]⁻ groups and F⁻ for O²⁻ has been made while the inherent structural merit of the parent compound has been maintained. As a result, BiFSeO₃ adopts the same NCS polar space group, Pnma, as that of BiOIO₃, however, it features a 3D framework rather than the layered backbone of BiOIO₃. The structure of BiFSeO₃ is constructed from 1D [Bif]²⁺ chains and the bridging [SeO₃]²⁻ groups through the Bi–O bonds. The seven-coordinated Bi³⁺ is bonded by five O²⁻ from five [SeO₃]²⁻ anionic groups and two F⁻ anions, which forms a severely distorted [BiO₂F₂] pentagonal bipyramid (Fig. 7). High-quality millimeter-sized BiFSeO₃ single crystals could be hydrothermally synthesized at 220 °C, which are stable up to 300 °C based on the TGA analysis. BiFSeO₃ has a larger band gap (3.83 eV) than BiOIO₃ (3.3 eV). Remarkably, BiFSeO₃ has very strong phase-matchable SHG efficiencies in both visible and NIR regions, which are about 13.5 times that of KDP (up to 5.40 μm). Theoretical calculations indicate that the contribution percentages of [SeO₃] and [BiO₂F₂] to the SHG tensor, d₃₁, are 62.8% and 37.1%, respectively. Thus, the observed strong SHG response of BiFSeO₃ should be attributed to the synergistic effect of both [SeO₃] and [BiO₂F₂] NLO-active groups.

RbTeMo₂O₈F. Single crystals of RbTeMo₂O₈F grown by a hydrothermal method at 230 °C are thermally stable up to 758 °C. Belonging to the polar NCS space group, Pn, the structure of RbTeMo₂O₈F features unique 2D [MoO₅F]_{a} layers composed of distinctive [MoO₂F] octahedra, [MoO₃] octahedra, and [TeO₄] units, in which both Mo⁶⁺ and Te⁴⁺ cations are in asymmetric coordination environments attributable to the SOJT effects (Fig. 8). RbTeMo₂O₈F displays a layered structure similar to that of NLO BaTeMo₂O₉. However, half of the [MoO₅F]_{a} groups in the [MoO₅F]_{a} layers of BaTeMo₂O₉ are substituted by partially fluorinated [MoO₂F] octahedra in RbTeMo₂O₈F, and Ba²⁺ cations residing in the interlayer space are replaced by Rb⁺ to make a charge balance. More importantly, the introduction of [MoO₂F] octahedra containing highly electronegative F⁻ not only enlarges the band gap of RbTeMo₂O₈F (3.63 eV) compared to that of BaTeMo₂O₉ (2.95 eV), but also leads to the ordered arrangement of [TeO₄] units, which in turn induces an enhanced macroscopic polarization and SHG response. The dipole moment calculations reveal that RbTeMo₂O₈F exhibits a much larger net dipole moment (13.32 D) than BaTeMo₂O₉ (5.50 D). Besides, RbTeMo₂O₈F displays the largest SHG responses (27× KDP@1064 nm, 2.2× KTP@2100 nm) among all the reported metal tellurites. The giant SHG responses can be attributed to the uniform alignment of the NLO-active units including [MoO₂F]_{a}, [MoO₃]_{a}, and [TeO₄] groups with the SHG contributions of 42.2%, 25.3%, and 29.7%, respectively, based on the theoretical calculations. Moreover, the compound also has a relatively wide IR transparent window (up to 5.40 μm) and a significant birefringence (0.263@546 nm) favorable for phase-matching in NLO processes. All the attributes collectively indicate that RbTeMo₂O₈F can be an outstanding candidate for Vis–NIR and mid-IR NLO materials. In addition to the above compounds, properties of other NLO metal oxyhalide selenites/tellurites such as Cs(TiOF)₃(SeO₃)₂, are also included in the review.
Bi$_2$(SeO$_3$)$_3$(Se$_2$O$_6$)F$_3$ and Ba(MoO$_2$F)$_2$(QO$_3$)$_2$ (Q = Se and Te) are also summarized in Table 1.

### 2.1.6 NLO metal oxyhalide iodates

ABi$_2$(IO$_3$)$_2$F$_3$ (A = K, Rb, and Cs). Isostructural ABi$_2$(IO$_3$)$_2$F$_3$ (A = K, Rb, and Cs) were synthesized by hydrothermal reactions.$^{35}$ Crystallizing in the monoclinic space group, $P2_1$, their structures are characterized by 2D $[\text{Bi}_2(\text{IO}_3)_2\text{F}_5]$ layers formed by $[\text{BiO}_2\text{F}_4]$ oxyfluoride groups, $[\text{BiF}_3]$ groups, and $[\text{IO}_3]$ groups (Fig. 9). All the constituting units display considerable structural distortions with polar features due to the lone pair electrons on Bi$^{3+}$ and I$^{5+}$ cations. The well-ordered arrangement of these polar groups in ABi$_2$(IO$_3$)$_2$F$_3$ (A = K, Rb, and Cs) finally results in strong SHG responses of 12, 9.5, and 7.5 times that of KDP at 1064 nm. Besides, the band gaps of ABi$_2$(IO$_3$)$_2$F$_3$ increase slightly from K to Rb to Cs (3.75, 3.78, and 3.84 eV, respectively). Thermal analyses indicate that KBi$_2$(IO$_3$)$_2$F$_5$ is stable up to 270 °C, while RBi$_2$(IO$_3$)$_2$F$_5$ and CsBi$_2$(IO$_3$)$_2$F$_5$ do not show any sign of decomposition until 240 °C. Considering the remarkable SHG efficiencies with the phase-matching behavior, relatively large band gaps, and wide transparency range (0.3–11 μm), ABi$_2$(IO$_3$)$_2$F$_5$ could be promising candidates for mid-IR NLO applications.

CsVO$_2$F(IO$_3$). The first alkali-metal vanadium oxyfluoride iodate, CsVO$_2$F(IO$_3$), has been synthesized hydrothermally.$^{46}$ Crystallizing in the polar orthorhombic space group, $Pna_2_1$, CsVO$_2$F(IO$_3$) features a novel 3D anionic framework, $[\text{VO}_5\text{F}]$ distorted octahedra and $[\text{IO}_3]$ trigonal pyramids (Fig. 10). The large magnitude of the out-of-center distortion of $[\text{VO}_5\text{F}]$ ($\Delta_d = 1.23$) is close to that of $[\text{VO}_5\text{F}]$ ($\Delta_d = 1.20$) in $\alpha$-Ba$_2$[$\text{VO}_2\text{F}_2$(IO$_3$)$_2$]IO$_3$.$^{47}$ CsVO$_2$F(IO$_3$) has a strong SHG response of 1.1 times that of KTP under 2.05 μm laser irradiation. Theoretical calculations reveal that the SHG contribution percentages of $[\text{VO}_5\text{F}]$, $[\text{IO}_3]$, and Cs$^+$ units are 62.18%, 36.05% and 1.55%, respectively. Thermal analyses indicate that the framework of the compound is stable up to 350 °C, which is relatively high for iodates. Although CsVO$_2$F(IO$_3$) has a relatively small band gap (2.39 eV), the material displays a high powder LDT of 107.9 MV cm$^{-2}$. In addition, it has a wide IR transparent range up to 10.5 μm based on the powder measurements, suggesting its potential NLO applications in the IR region. In addition to the above compounds, characteristics of other NLO metal oxyhalide iodates such as $\alpha$- and $\beta$-Ba$_2$[VO$_2$F$_2$(IO$_3$)$_2$]IO$_3$,$^{47}$ (NH$_4$)$_2$Bi$_2$(IO$_3$)$_2$F$_5$,$^{48}$ Bi$_2$Te(IO$_3$)$_2$OCl,$^{48}$ Bi[IO$_3$]F$_2$,$^{50}$ Bi$_2$TeF$_6$(IO$_3$)$_2$,$^{41}$ Sn(IO$_3$)$_2$F$_2$,$^{52}$ CsZrF$_4$(IO$_3$)$_2$,$^{53}$ K$_3$(W$_2$O$_8$F$_3$(IO$_3$)$_2$)$^{54}$ and CdIO$_3$F$^{57}$ are also summarized in Table 1.

### 2.2 “Pure” metal oxyhalides with single halogen type for NLO materials

#### 2.2.1 NLO transition metal oxyhalides

KWO$_3$F. Very recently, single crystals of KWO$_3$F were synthesized under hydrothermal conditions at 240 °C.$^{56}$ The compound crystallizes in the orthorhombic polar space group, $Amma$. The W(vi) atom is six-coordinated by mixed ligands to form a [WO$_3$F] distorted octahedron owing to the SOJT effect. Note that the [WO$_3$F] octahedron has not been reported previously in other transition metal oxyhalides. While the W–O distances are 1.735–2.034 Å, that of W–F is 2.141 Å, which results in the magnitude of the out-of-center distortion ($\Delta_d$) value of 0.65 for the [WO$_3$F] octahedron. Each [WO$_3$F] octahedron further polymerizes through corner-sharing with [WO$_3$F] anionic layers that are stacked along the [001] direction (Fig. 11). Interestingly, the distorted octahedra are perfectly aligned in the layer, which is beneficial to produce a large SHG effect and suitable birefringence for phase-matching. Experimental results reveal that KWO$_3$F is thermally stable up to 350 °C in air. The compound also exhibits a large phase-matchable SHG response (3× KDP), large birefringence (0.088@1064 nm), wide IR transparent window (up to 10 μm), and relatively high powder LDT (129.7 MW cm$^{-2}$).

In addition, quite a few “pure” $d^0$O$^{10}$ transition metal oxyfluorides with NLO properties, such as Sr$_2$Nb$_2$O$_7$F$_{12}$·2H$_2$O,$^{57}$...
StMoO$_2$F$_4$, $\alpha$-BaMoO$_3$F$_4$, PbMoO$_4$F$_4$, KMoO$_2$F$_3$, NaVO$_2$, and KNaNbOF$_5$ have also been discovered recently. However, most of them exhibit relatively small SHG responses ($\leq 1 \times$ KDP) possibly attributed to the relatively small distortions or the unfavorable arrangements of their transition metal--oxyfluoride functional units. It is worth noting that the Pan group recently performed systematic calculations and analyses of d$^0$ transition metal oxyfluorides with NCS structures. Excitingly, they proposed that Ba$_3$MoO$_4$F$_4$ and Ba$_3$WO$_4$F$_4$ with the well-arranged anionic groups can be promising mid-IR NLO materials based on the calculations of NLO properties, in which the expected excellent properties of the materials include large NLO coefficients (corresponding to strong SHG responses, $10 \times$ KDP), wide band gaps, large IR absorption edges (10 µm), and large birefringences. This theoretical study can be an excellent guideline for the design and screening of novel mid-IR NLO materials in the transition metal oxyfluoride system.

2.2.2 NLO post-transition metal oxyhalides

$\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ The combination of heavy Pb$^{2+}$ with possible lone pair electrons and highly electronegative Cl$^-$ in oxides led to the discovery of a novel NLO material, $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$. Remarkably, single crystals of $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ were grown from the stoichiometric melt of PbO and PbCl$_2$ through a facile spontaneous crystallization in an open system. The size of obtained crystals is up to $7 \times 2 \times 2$ mm$^3$. $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ crystallizes in the orthorhombic polar space group, $\text{Fmm}2$, featuring a complex 3D infinite chains occupied by (Pb1)-Pb(7) sites are coordinated by 2O$_2$- and Br$^-$ ions with strongly asymmetric characteristics while those in the Pb(8) sites are coordinated exclusively by Cl$^-$ and Br$^-$. Polycrystalline samples of the compounds were all synthesized by a standard solid-state reaction while the single crystals have been grown from high temperature solutions using self-fluxes of xPbCl$_2$-yPbBr$_2$. Inspiringly, large centimeter-sized (up to $2.9 \times 1.3 \times 0.5$ cm$^3$) crystals of $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ were successfully obtained with the aid of the top-seeded solution growth (TSSG) technique after the continuous optimization of growth parameters. Experimental results manifest that the three materials can satisfy all the fundamental criteria of high-performance mid-IR NLO materials.

3. NLO metal oxyhalides with mixed halogen anions

3.1 $\text{Pb}_{17}\text{O}_8\text{Cl}_18$, $\text{Pb}_{13}\text{O}_6\text{Cl}_7\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$

Based on the analyses that lead mixed oxyhalides could be a new promising branch for mid-IR NLO materials, systematic exploration in the PbO-PbCl$_2$-PbBr$_2$ system has been performed. The effort led to the discovery of the first examples of NLO lead mixed oxyhalides, namely, $\text{Pb}_{13}\text{O}_6\text{Cl}_7\text{Br}_7$, $\text{Pb}_{17}\text{O}_8\text{Cl}_18$, and $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$. Isomorphic $\text{Pb}_{17}\text{O}_8\text{Cl}_18$, $\text{Pb}_{13}\text{O}_6\text{Cl}_7\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ all crystallize in the polar space group, $\text{Fmm}2$. Their structures are similar to that of $\text{Pb}_{17}\text{O}_8\text{Cl}_18$ in terms of the arrangement of oxygen-centered [OPb$_2$]$_2$+ infinite chains along the [010] direction (Fig. 12). In their structures, Pb$^{2+}$ cations occupying the Pb(1)-Pb(7) sites are coordinated by 2O$_2$- + mCl$^-$ + nBr$^-$ anions with strongly asymmetric characteristics while those in the Pb(8) sites are coordinated exclusively by Cl$^-$ and Br$^-$. Polycrystalline samples of the compounds were all synthesized by a standard solid-state reaction while the single crystals have been grown from high temperature solutions using self-fluxes of xPbCl$_2$–yPbBr$_2$. Inspiringly, large centimeter-sized (up to $2.9 \times 1.3 \times 0.5$ cm$^3$) crystals of $\text{Pb}_{17}\text{O}_8\text{Cl}_18$, $\text{Pb}_{13}\text{O}_6\text{Cl}_7\text{Br}_7$, and $\text{Pb}_{13}\text{O}_6\text{Cl}_4\text{Br}_{10}$ were successfully obtained with the aid of the top-seeded solution growth (TSSG) technique after the continuous optimization of growth parameters. Experimental results manifest that the three materials can satisfy all the fundamental criteria of high-performance mid-IR NLO materials.
including strong SHG efficiencies (0.9, 0.8, and 0.6×
AgGaS2@2.09 μm, respectively) with phase-matchability, wide
band gaps (3.21, 3.13, and 3.05 eV, respectively), and broad IR
transparency up to 14 μm. Among them, Pb13O6Cl9Br5 has
shown a high LDT on a single crystal (439 MW cm−2, 14.6×
AgGaS2) and revealed the best overall properties. This study
indicates that by incorporating different types of halogen
anions in one compound, the compositional diversity of lead
oxyhalides can be increased compared to those with a single
halogen type (F−, Cl−, Br−, or I−). It is believed that the provided
feasible approach would promote the synthesis and the large
crystal growth of more novel metal oxyhalides for NLO
materials.

3.2 Pb18O8Cl15I5

Through targeted element-composition design and experience-
based discovery synthesis, a novel NLO lead mixed oxyhalide,
Pb18O8Cl15I5 was successfully obtained by our group.65 Aiming
at developing high-performance NLO materials for IR applica-
tions, the design strategy is based on the following aspects: (1)
oxide-based materials have convincing advantages in crystal
growth and optical properties; (2) the employment of a stereo-
chemically active heavy metal lone pair cation, Pb2+, is not only
able to expand the IR transparency, but also to strengthen the
SHG response; (3) the selection of a highly electronegative
halide, Cl− is conducive to enlarge the band gap and thus
subsequently to achieve a high LDT; (4) by introducing the
second halogen anion, I−, which has significant differences in
size and polarizability with Cl− and O2−, the coordination
flexibility and diversity of Pb2+ can be increased. Therefore, the
produced [PbOClnIi] polyhedra with a considerable distortion
would be beneficial to obtain enhanced NLO properties in a
material. Pb18O8Cl15I5 crystallizes in the monoclinic polar
space group, Cc. As expected, Pb2+ cations exhibit diverse
asymmetric coordination geometries and form exceptional
polyhedra such as [PbOCl5I8], [PbO3Cl2I4], [PbO2Cl4I2], and
[PbCl4I2]. More interestingly, Pb18O8Cl15I5 not only possesses
an NCS polar structure, but also exhibits the unprecedented
structure featuring two different dimensional types of oxocen-
tered Pb−O groups, i.e., 0D [O−Pb8]8+ clusters and 1D [O−Pb2]2+
chains (Fig. 13). Single crystals of Pb18O8Cl15I5 were grown by
the flux method in an open system at a temperature below
400 °C. By employing the TSSG technique, centimeter-sized
Pb18O8Cl15I5 crystals (up to 3.2 × 1.1 × 0.6 cm3) have been
successively obtained in a short development cycle. Intrigu-
ingly, Pb18O8Cl15I5 displays a very strong powder phase-
matching SHG response (1.05× AgGaS2), applicable birefrin-
gence (0.086@636 nm), high single-crystal LDT (255 MW cm−2,
8.5× AgGaS2), and the widest IR transparency (up to 16.0 μm)
among oxide-based materials, which are superior to those of
the commercial IR NLO material, AGS. The excellent overall
properties as well as the great advantage in crystal growth unam-
biguously demonstrate that Pb18O8Cl15I5 is an excellent
candidate for high-performance mid-IR NLO materials. More-
over, Pb18O8Cl15I5 represents the first artificial metal oxyhalide
with the combination of Cl− and I−, revealing that the structural
and functional diversity of metal oxyhalides can be greatly
increased through the incorporation of different kinds of halogen
anions.

3.3 CsZn3BO3FCl

Single crystals of CsZn3BO3FCl were synthesized via the high
temperature solution method.66 Crystallizing in the polar space
group, R3, CsZn3BO3FCl contains [Zn3BO3FCl] layers that resemble
the [Be2BO3F2] layers in KBBF (Fig. 14). Note that CsZn3BO3FCl is the first example in the KBBF family with mixed
halogen anions. In the structure, F and Cl occupy different
individual crystallographic sites; thus, [Zn(1)O3F] and [Zn(2)
O3Cl] tetrahedra are formed, respectively, in CsZn3BO3FCl.
Interestingly, two other compounds with single type halogen
anions, isostructural CsZn3BO3F2 and CsZn3BO3Cl2 crystallize
in the nonpolar NCS space group, R32. CsZn3BO3FCl reveals
more enhanced SHG responses (3.5× KDP@1064 nm, 0.58×
BBO@532 nm) compared to those of CsZn3BO3F2 (3.2×
KDP@1064 nm, 0.54× BBO@532 nm) and CsZn3BO3Cl2 (2.8×
KDP@1064 nm, 0.50× BBO@532 nm), which is probably
induced by the mixed halogen anions, F− and Cl− with a large
electronegativity difference in CsZn3BO3FCl. Theoretical real-
space atom-cutting analyses of the SHG effect reveal that the contributions of [ZnO3X] [X = F and Cl] and [BO3] are
comparable while Cs+ makes little contribution. Thermal analyses
indicate that the compound melts incongruently and is stable
up to 677 °C. Moreover, the compound has a very short UV
cutoff edge (<190 nm), indicating that CsZn3BO3FCl could be a
potential UV and DUV NLO material.

3.4 Cs2Pb2(CH3COO)2Br3I5

By the partial substitution of Br− anions in Cs2Pb2(CH3COO)2−
Br3 for I−, a new isostructural compound, Cs2Pb2(CH3COO)2−
Br2I2, has been obtained under mixed-solvothermal conditions.67 Different from Cs2Pb2(CH4COO)2Br5 with single
halogen type, the structure of Cs2Pb2(CH3COO)2Br2I2 contains

Fig. 13 Crystal structure of Pb18O8Cl15I5 viewed along the a-axis (Pb–Cl and Pb–I bonds have been omitted for clarity).
rare Pb–mixed-oxyhalide polyhedra, [PbO2Br2I2] (Fig. 15), which are severely distorted and exhibit a larger polarizability. Consequently, the compound displays an enhanced SHG response (9\times\text{KDP}) and enlarged birefringence (0.27@1064 nm) compared to Cs3Pb2(CH3COO)2Br5 (4\times\text{KDP}, 0.15@1064 nm) and Cs3Pb2(CH3COO)2I5 (8\times\text{KDP}, 0.26@1064 nm). The results manifest that the well-arranged PbBr2I2O2 polyhedra composed of Pb2+ with the stereochemically active lone pair and multiple types of anions (O2\textsuperscript{2−}, Br\textsuperscript{−}, and I\textsuperscript{−}) with different ionic radius, electronegativity, and coordination capability, can not only enhance the polarizability to strengthen the SHG response, but also improve the anisotropy to enlarge the birefringence of a material.

3.5 Pb\textsubscript{2}TiOF(SeO\textsubscript{3})\textsubscript{2}Cl and its analogs

Pb\textsubscript{2}TiOF(SeO\textsubscript{3})\textsubscript{2}Cl was discovered by a hydrothermal synthesis during the efforts of introducing the halogen anions into the Pb-d\textsuperscript{0} transition metal–selenite system.\textsuperscript{67} The compound crystallizes in the polar monoclinic space group, P2\textsubscript{1}, exhibiting a novel 3D network constructed from 1D [ClPb\textsubscript{2}]\textsuperscript{3+} cationic chains and 1D [TiO\textsubscript{5}F\textsubscript{2}]\textsuperscript{−} anionic chains that are composed of Ti\textsuperscript{4+}–oxyfluoride group, [TiO\textsubscript{2}F\textsubscript{6}] distorted octahedra, and [SeO\textsubscript{3}] groups (Fig. 16). The calculated magnitude of the out-of-center distortion (\(d_0\)) is 0.6183. The Pb atoms in Pb\textsubscript{2}TiOF(SeO\textsubscript{3})\textsubscript{2}Cl have two kinds of coordination environment, producing Pb–oxychloride [PbO\textsubscript{6}Cl\textsubscript{2}] polyhedra and Pb–mixed-oxyhalide [PbO\textsubscript{5}Cl\textsubscript{2}F\textsubscript{2}] polyhedra, which are all severely distorted due to the presence of the lone pair electrons on Pb\textsuperscript{2+}. Powder SHG tests reveal that Pb\textsubscript{2}TiOF(SeO\textsubscript{3})\textsubscript{2}Cl has strong phase-matchable SHG responses of 9.6 times that of KDP at 1064 nm and 0.65 times that of KTP at 2050 nm. The collaborative polarizations from the asymmetric NLO-active units, including [PbO\textsubscript{5}Cl\textsubscript{2}F\textsubscript{2}], [PbO\textsubscript{6}Cl\textsubscript{2}], [TiO\textsubscript{5}F\textsubscript{2}], and [SeO\textsubscript{3}], should be responsible for the large SHG effect in Pb\textsubscript{2}TiOF(SeO\textsubscript{3})\textsubscript{2}Cl. It is interesting to note that another isostructural compound, Pb\textsubscript{2}NbO\textsubscript{2}(SeO\textsubscript{3})\textsubscript{2}Cl, displays a much weaker SHG response (2.3\times\text{KDP}).\textsuperscript{67} For Pb\textsubscript{2}NbO\textsubscript{2}(SeO\textsubscript{3})\textsubscript{2}Cl, the main structural differences are the replacement of [TiO\textsubscript{5}F\textsubscript{2}], [PbO\textsubscript{5}Cl\textsubscript{2}F\textsubscript{2}], and [PbO\textsubscript{6}Cl\textsubscript{2}] with [NbO\textsubscript{6}], [PbO\textsubscript{6}Cl\textsubscript{2}], and [PbO\textsubscript{5}Cl\textsubscript{2}]. Therefore, the introduction of a second type halogen anion, F\textsuperscript{−}, is likely to induce a stronger SHG response, which has been subsequently demonstrated by analyzing the band structures of the two compounds based on the first-principles calculations. Remarkably, Liu et al. have successfully synthesized the bromide analog, Pb\textsubscript{2}TiFO(SeO\textsubscript{3})\textsubscript{2}Br, with a larger SHG response (10\times\text{KDP}), which is probably more difficult to obtain in the synthesis due to the increased difference between Br\textsuperscript{−} and F\textsuperscript{−}. Similar to the coordination in Pb\textsubscript{2}TiFO(SeO\textsubscript{3})\textsubscript{2}Cl, [TiO\textsubscript{2}F\textsubscript{6}], [PbO\textsubscript{6}Br\textsubscript{2}], and [PbO\textsubscript{6}Br\textsubscript{2}F\textsubscript{2}] polyhedra are observed in Pb\textsubscript{2}TiFO(SeO\textsubscript{3})\textsubscript{2}Br, however, we noticed that the Pb–mixed-oxyhalide unit, [PbO\textsubscript{6}Br\textsubscript{2}F\textsubscript{2}], combining F\textsuperscript{−} and Br\textsuperscript{−} is quite rare, except for the case in another analog, Pb\textsubscript{2}GaF\textsubscript{2}(SeO\textsubscript{3})\textsubscript{2}Br, which displays an SHG response which is 4.5 times that of KDP.\textsuperscript{69} In addition, through the band engineering strategy achieved by the aliovalent substitution, isomorphic Pb\textsubscript{2}GaF\textsubscript{2}(SeO\textsubscript{3})\textsubscript{2}Cl has also been obtained, which exhibits the widest band gap (4.32 eV) among all the reported phase-matchable NLO selenites while maintaining a relatively large SHG response (4.5\times\text{KDP}).\textsuperscript{70}
4. Conclusions and outlook

In summary, the recent significant advancements of NLO metal oxyhalides have been reviewed. Forty-eight NLO metal oxyhalides with various metal-oxyhalide functional units have been presented in Tables 1 and 2. Compared to the traditional metal-oxide functional units, metal-oxyhalide units combining O$_2^-$ and X$^-$ (X = F, Cl, Br, and I) clearly result in diverse metal-centered polyhedra with considerable distortions, especially when more than one type of X$^-$ is incorporated. These distorted metal-oxyhalide polyhedra can serve as both NLO-active units and birefringence-active units, which have been demonstrated to be helpful in realizing strong SHG responses and large birefringences in NLO materials. Besides, the band gaps, SHG responses, and even other properties of metal oxyhalides can be possibly tuned based on the same or similar structural configurations by choosing different halogen anions, as can be seen in Pb$_2$B$_5$O$_9$X (X = Cl, Br, and I), Cs$_3$Pb$_2$(CH$_3$COO)$_2$X$_3$ (X = Br and I), Cs$_3$Pb$_2$(CH$_3$COO)$_2$Br$_2$I$_2$, Pb$_3$O$_2$Cl$_2$Br$_2$, Pb$_3$O$_2$Cl$_2$Br$_2$, Cs$_3$Pb$_2$(IO$_3$)$_2$F$_5$, and Pbl$_{10}$O$_8$Cl$_4$Br$_10$. It is worth noting that the participation of additional halide compounds exhibiting strong SHG responses. The strong is a very e

Table 2: Space groups, metal–oxygen unit types, and key properties of NLO metal oxyhalides with mixed halogen anions

<table>
<thead>
<tr>
<th>No.</th>
<th>Metal–oxygen unit type</th>
<th>Space group</th>
<th>Key properties of NLO metal oxyhalides with mixed halogen anions</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pb$_2$Cl$_2$I$_2$(SeO$_3$)$_2$ (ref. 61)</td>
<td>Pm-3m</td>
<td>IR cutoff edge: 1.34 µm (calc.)</td>
</tr>
<tr>
<td>2</td>
<td>Pb$_2$Cl$_2$I$_2$(SeO$_3$)$_2$ (ref. 61)</td>
<td>Pm-3m</td>
<td>SHG: 4.32 V/m</td>
</tr>
<tr>
<td>3</td>
<td>Pb$_2$Cl$_2$I$_2$(SeO$_3$)$_2$ (ref. 61)</td>
<td>Pm-3m</td>
<td>Birefringence: 0.196 @ 1064 nm (exp.)</td>
</tr>
<tr>
<td>4</td>
<td>Pb$_2$Cl$_2$I$_2$(SeO$_3$)$_2$ (ref. 61)</td>
<td>Pm-3m</td>
<td>LDT: 0.65 @ 1064 nm (exp.)</td>
</tr>
</tbody>
</table>

* The SHG intensity was measured at 1064 nm using KDP as the reference and at 1.39 µm when using KTP or AGS as the reference. The IR cutoff edge was preliminarily measured on powder samples. The LDT was estimated on single crystals.
mixed halogen anions, it is found that the targeted combination of different halogen anions in one compound has become a feasible and compelling way to produce more NLO metal oxyhalides with increased compositional and structural diversification. However, the development of NLO metal oxyhalides with mixed halogen anions is still in the primary stage.

In terms of the application prospects, NLO metal oxyhalides with additional anionic groups can be promising candidates for NLO materials working beyond 5 μm atmospheric window if their large single crystals can be successfully grown in the future. However, the combination of various anionic groups in one compound usually increases the difficulty in large single crystal growth. For mid-IR NLO materials working beyond 5 μm, a more careful chemical composition design should be taken into consideration because the introduction of relatively light atoms needs to be avoided in order to achieve a wider IR transparency. In this aspect, the emerging heavy metal mixed oxyhalides without traditional metal–oxide anionic groups, for example, Pb$_{18}$O$_8$Cl$_{15}$I$_5$ and Pb$_{11}$O$_6$Cl$_3$Br$_5$, have manifested unprecedented advantages in both structural diversity and functionality compared to other oxide-based compounds for mid-IR NLO materials. More inspiringly, centimeter-sized single crystals of Pb$_{18}$O$_8$Cl$_{15}$I$_5$ and Pb$_{11}$O$_6$Cl$_3$Br$_5$ have been successfully grown by a feasible method in a relatively short development cycle. Therefore, considering the excellent potential in structural diversity and tunability as well as the consequently fascinating overall properties, we firmly believe that more novel metal oxyhalides with additional anionic groups and metal oxyhalides with mixed halogen anions will be discovered, and this emerging branch can provide very competitive candidates for high-performance NLO materials, especially in Vis–NIR and mid-IR regions.

Author contributions
Both authors contributed to the conceptualization, writing, and editing of the manuscript.

Conflicts of interest
There are no conflicts to declare.

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Notes and references