

Synthesis, Crystal and Electronic Structures, Linear and Nonlinear Optical Properties, and Photocurrent Response of Oxyhalides CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W)

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## **Abstract**

Four heteroanionic oxyhalides, CeClMoO<sub>4</sub>, CeBrMoO<sub>4</sub>, CeClWO<sub>4</sub>, and CeBrWO<sub>4</sub>, have been studied as multifunctional materials, which combine good second harmonic generation (SHG) response and photocurrent signals. Millimeter-sized CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) crystals were grown by halide salt flux. The crystal structure of CeHaVIO<sub>4</sub> crystals was accurately determined by single crystal X-ray diffraction. CeClMoO<sub>4</sub>, CeBrMoO<sub>4</sub>, and CeBrWO<sub>4</sub> are isostructural to each other, which crystallize in the acentric LaBrMoO<sub>4</sub> structure type. CeClWO<sub>4</sub> crystallizes in a new structure type with unit cell parameters of  $a=19.6059(2)$  Å,  $b=5.89450(10)$  Å,  $c=7.80090(10)$  Å,  $\beta=101.4746(8)^\circ$ . The bandgaps of CeHaVIO<sub>4</sub> fall into the range of 2.8(1)-3.1(1) eV, which are much smaller than the isotypic LaHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) of 3.9(1)-4.3(1) eV. The narrowing of bandgaps in CeHaVIO<sub>4</sub> originates from the presence of partially filled *4f* orbitals of cerium atoms, which was confirmed by density functional theory (DFT) calculations. The moderate bandgaps make CeHaVIO<sub>4</sub> suitable for infrared nonlinear optical applications (IR NLO). CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> exhibit moderate SHG responses of  $0.58\times$  AGS and  $0.46\times$  AGS, respectively, which are both type-I phase-matching materials. Moderate SHG response, easy-growth of crystals, high ambient stability, and type-I phase-matching behavior set CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> as great materials for IR NLO applications. CeHaVIO<sub>4</sub> films also exhibited good

photocurrent response upon light radiation. This work demonstrates the rich structure chemistry of the REHaVIO<sub>4</sub> (RE=Y, La-Lu, Ha=Cl, Br; VI=Mo, W) family and the potential presence of more multifunctional materials.

## Introduction

Infrared nonlinear optical (IR NLO) materials have been vigorously studied due to their irreplaceable roles in solid-state lasers, which are utilized to expand infrared laser frequency via the second harmonic generation process<sup>1-14</sup>. The options for IR NLO materials are still limited to a few commercial materials such as ZnGeP<sub>2</sub>, AgGaS<sub>2</sub>, and AgGaSe<sub>2</sub>. These commercial materials cannot be utilized to cover the full spectrum range of 3-25  $\mu\text{m}$  due to intrinsic limitations such as low laser damage thresholds (AgGaS<sub>2</sub>, and AgGaSe<sub>2</sub>)<sup>15</sup> and double-photon absorption (ZnGeP<sub>2</sub>)<sup>16</sup>. A state-of-the-art IR NLO material should crystallize in an acentric structure and, ideally, balance a large second harmonic generation coefficient (SHG,  $d_{ij} > \text{AgGaS}_2$ ), moderate birefringence ( $\Delta n$ ) for phase matchability, high laser damage threshold (LDT,  $> \text{AgGaS}_2$ ), large bandgap for good transmission range ( $> 3.5 \text{ eV}$ ) and good thermal-, air-, and chemical stability, all of which are nearly impossible for many systems. Balancing these properties to satisfy these criteria is not a simple task due to the fact that many of these parameters are intrinsically correlated<sup>17-29</sup>. For example, in general, a material with a large bandgap should have a high LDT, but the SHG coefficients would be expected to be low. Inversely, small bandgap materials are more likely to have large SHG coefficients, but with the price of sacrificing LDT<sup>17, 21, 29-31</sup>. Hence, finding a chemical system, which meets all criteria, is important and challenging.

Oxyhalides, which constitute two anions of oxygen and halogen, have been emerging as important NLO materials, especially for covering visible or ultraviolet spectrum range, but rarely used for IR NLO applications<sup>32-42</sup>. There are two major reasons for this: first, the presence of metal-oxygen bonds, whose intrinsic vibrations are over the spectrum ranges of 3-5  $\mu\text{m}$  and 8-12  $\mu\text{m}$ , resulting in high optical absorption of desired IR spectrum range; second, the strong ionic metal-halogen interactions, which have tight bonding of valence electrons around anions, generating very large bandgaps<sup>32-42</sup>. A very large bandgap is usually accompanied by a small SHG response. Hence, a good strategy to "push" oxyhalides into the IR spectrum range is necessary. One successful strategy to create good oxyhalide IR NLO materials is to incorporate heavy metals like Pb, such as, Pb<sub>17</sub>O<sub>8</sub>Cl<sub>18</sub><sup>43</sup>, Pb<sub>13</sub>O<sub>6</sub>Cl<sub>14</sub>Br<sub>10</sub><sup>44</sup>, Pb<sub>18</sub>O<sub>8</sub>Cl<sub>15</sub>I<sub>5</sub><sup>45</sup>. Another good method to employ oxyhalides as

IR NLO materials is to add more anions such as  $[\text{Ba}_2\text{F}_2][\text{Ge}_2\text{O}_3\text{S}_2]$  <sup>46</sup>. All these strategies have successfully suppressed the bandgaps of inorganic solids, leading to good transmission over the IR spectrum range while maintaining high SHG responses. In this work, we attempted a new strategy of utilizing Ce's partially occupied 4*f* orbitals to narrow the bandgaps of oxyhalides  $\text{CeHaVIO}_4$  into the IR spectrum range and succeeded. For instance,  $\text{CeBrWO}_4$  is isostructural to  $\text{LaBrWO}_4$ . By replacing La by Ce, the bandgap was narrowed from 4.2(1) eV to 2.8(1) eV for  $\text{LaBrWO}_4$  and  $\text{CeBrWO}_4$ , respectively. The synthesis, crystal and electronic structures, and linear and nonlinear optical properties of oxyhalides  $\text{CeHaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) are reported in this work.  $\text{CeBrMoO}_4$  is found to be a good IR NLO material with balanced properties ( $E_g=3.0(1)$  eV, SHG:  $0.58\times$  AGS). Therefore, this work finds a new method to modulate oxyhalides as potential IR NLO materials.

## Experimental Details

**Synthesis and crystal growth:** Raw reactants in this work were used as received without further processing:  $\text{CeBr}_3$  (Thermo Fisher Scientific, 99.9%),  $\text{CeCl}_3$  (Thermo Fisher Scientific, 99.9%),  $\text{Ce}_2\text{O}_3$  (MSE Supplies, 99.9%),  $\text{MoO}_3$  (Alfa Aesar, 99.5 %),  $\text{WO}_3$  (Alfa Aesar, 99.8%),  $\text{NaBr}$  (Thermo Fisher Scientific, 99+%),  $\text{NaCl}$  (Sigma-Aldrich, anhydrous, 99.5%). All these reactants were stored in an argon-filled glovebox and the moisture and oxygen levels of the glovebox were kept below 0.5 ppm.

**$\text{CeClVIO}_4$  (VI=Mo, W):** Flux  $\text{CeCl}_3/\text{NaCl}$  was utilized to grow crystals of  $\text{CeClVIO}_4$  (VI=Mo, W). 0.4 g of  $\text{CeCl}_3$ ,  $\text{Ce}_2\text{O}_3$ , and  $\text{VIO}_3$  (VI=Mo, W) mixed in a molar ratio of 1:1:3 were loaded into a carbonized silica tube first. Then, 0.4 g of flux of  $\text{CeCl}_3/\text{NaCl}$  mixed in a molar ratio of 1:2 were loaded to cover the top of reactants. The silica tubes were transferred out of glovebox and sealed by a torch under a vacuum of  $10^{-2}$  Torr. The tube was heated from room temperature to 820 °C in 10 hrs and held for 168 hrs before naturally cooling down. The crystals were collected after the flux was removed by DI water.  **$\text{CeBrVIO}_4$  (VI=Mo, W):** A similar synthetic routine was employed with  $\text{CeBr}_3/\text{NaBr}=1:2$  as flux. 0.4 g reactants of  $\text{CeBr}_3$ ,  $\text{Ce}_2\text{O}_3$ , and  $\text{VIO}_3$  (VI=Mo, W) mixed in a molar ratio of 1:1:3 were covered by 0.4 g flux. The temperature profile of  $\text{CeBrVIO}_4$  (VI=Mo, W) was identical to  $\text{CeClVIO}_4$  (VI=Mo, W). The crystals were collected after the flux was washed away by DI water. The optical microscope photos of crystals of  $\text{CeHaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) are shown in **Figure S1**. All samples in this work are stable in air for a long time.

The mixed-cation compounds of  $(\text{La}_{0.5}\text{Ce}_{0.5})\text{HaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) were grown by using the following equations:  $3(\text{La}_{0.5}\text{Ce}_{0.5})\text{HaVIO}_4 = 0.5\text{LaHa}_3 + 0.5\text{CeHa}_3 + 0.5\text{Ce}_2\text{O}_3 + 0.5\text{La}_2\text{O}_3 + 3\text{VIO}_3$  with flux of  $\text{CeHa}_3/\text{LaHa}_3/\text{NaHa} = 0.5:0.5:2$ , where Ha=Cl, Br and VI=Mo, W. The temperature profile of mixed-cation compounds was the same as the pristine compounds.

**Single Crystal X-ray Diffraction:** Crystals of  $\text{CeHaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) were manually picked up under an optical microscope and mounted to the Rigaku XtaLAB Synergy-I instrument. The data collection was performed at 290 (5) K. The data collection and integration were done by CrysAlis<sup>Pro</sup> Software (Agilent Technologies, XRD Products; CrysAlis Pro; Agilent Technologies, Inc). The structural solution and refinement were done with Jana2006<sup>47</sup>. Details of the data collection and structure refinement are provided in **Table 1**. Atomic coordinates and selected bond distances are listed in **Tables S1** and **S2**. Crystallographic data for  $\text{CeHaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) have been deposited to the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge by quoting the depository numbers CCDC- 2302882 ( $\text{CeClMoO}_4$ ), CCDC- 2302884 ( $\text{CeClWO}_4$ ), CCDC- 2302881 ( $\text{CeBrMoO}_4$ ), and CCDC- 2302883 ( $\text{CeBrWO}_4$ ) .

**Lab powder X-ray Diffraction:** Powder X-ray diffraction data were collected at room temperature using a Rigaku Mini Flex 6G diffractometer with Cu-K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) in the range  $2\theta = 10^\circ - 80^\circ$ , at a scan step of  $0.04^\circ$  with ten seconds exposure time.

**UV-Vis Measurements:** Diffuse-reflectance spectra were recorded at room temperature by a PERSEE-T8DCS UV-Vis spectrophotometer equipped with an integration sphere in the wavelength range of 230–850 nm. The reflectance data, R, were recorded and converted to the Kubelka-Munk function,  $f(R) = (1-R)^2/(2R)^{-1}$ . Tauc plots,  $(\text{KM} \cdot E)^2$  and  $(\text{KM} \cdot E)^{1/2}$ , were applied to estimate direct and indirect bandgaps, respectively.

**Second Harmonic Generation Measurements:** Using the Kurtz and Perry method,<sup>48</sup> powder SHG responses of  $\text{CeHaVIO}_4$  (Ha=Cl, Br; VI=Mo, W) compounds were investigated by a Q-switch laser (2.09  $\mu\text{m}$ , 3 Hz, 50 ns) with various particle sizes, including 38.5–54, 54–88, 88–105, 105–150, and 150–200  $\mu\text{m}$ .. Polycrystalline lab-synthesized  $\text{AgGaS}_2$  (AGS) was also sieved into similar particle sizes for SHG efficiency comparison. A short pass filter was placed in front of the photomultiplier tube to prevent scattered 1064 nm photons from being detected.

**Table 1.** Refined crystallographic parameters of CeClMoO<sub>4</sub>, CeClWO<sub>4</sub>, CeBrMoO<sub>4</sub>, and CeBrWO<sub>4</sub> from single crystal X-ray diffraction.

| Compound                                                              | CeClMoO <sub>4</sub>          | CeClWO <sub>4</sub>      | CeBrMoO <sub>4</sub> | CeBrWO <sub>4</sub> |
|-----------------------------------------------------------------------|-------------------------------|--------------------------|----------------------|---------------------|
| <b>Formula weight</b>                                                 | 335.5                         | 423.4                    | 380                  | 467.9               |
| <b>Crystal color</b>                                                  | translucent light orange      | translucent light yellow | translucent yellow   | translucent orange  |
| <b>Temperature (K)</b>                                                | 296.97                        | 297.6(7)                 | 296.36               | 296.4               |
| <b>Radiation, wavelength</b>                                          | Mo-K $\alpha$ , 0.71073 Å     |                          |                      |                     |
| <b>Crystal system</b>                                                 | Monoclinic                    |                          |                      |                     |
| <b>Space group</b>                                                    | <i>P</i> 1 <i>c</i> 1 (No. 7) |                          |                      |                     |
| <b>a(Å)</b>                                                           | 9.55135(6)                    | 19.6059(2)               | 9.77746(9)           | 9.87827(7)          |
| <b>b(Å)</b>                                                           | 5.79301(5)                    | 5.89450(10)              | 5.82090(5)           | 5.92232(3)          |
| <b>c(Å)</b>                                                           | 7.94951(9)                    | 7.80090(10)              | 8.03217(7)           | 7.93937(5)          |
| <b><math>\beta</math> (°)</b>                                         | 90.0140(7)                    | 101.4746(8)              | 90.0106(7)           | 90.0083(6)          |
| <b>V (Å<sup>3</sup>)</b>                                              | 439.851(7)                    | 883.51(2)                | 457.143(11)          | 464.473(11)         |
| <b>Z</b>                                                              | 4                             | 8                        | 4                    | 4                   |
| <b>D<sub>c</sub> (g cm<sup>-3</sup>)</b>                              | 5.0665                        | 6.3665                   | 5.5207               | 6.6907              |
| <b><math>\mu</math> (mm<sup>-1</sup>)</b>                             | 13.557                        | 36.679                   | 21.201               | 42.913              |
| <b>F(000)</b>                                                         | 596                           | 1448                     | 668                  | 796                 |
| <b>Flack</b>                                                          | 0.292(16)                     | 0.269(12)                | 0.033(18)            | 0.266(15)           |
| <b>Parameter</b>                                                      |                               |                          |                      |                     |
| <b>R<sub>1</sub>, wR<sub>2</sub> (all data)</b>                       | 0.0138, 0.0182                | 0.0229, 0.0294           | 0.0157, 0.0193       | 0.0211, 0.0256      |
| <b>R<sub>1</sub>, wR<sub>2</sub> (I &gt; 2<math>\sigma</math>(I))</b> | 0.0136, 0.0181                | 0.0257, 0.0298           | 0.0157, 0.0194       | 0.0208, 0.0255      |

$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $wR_2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$ , and  $w = 1 / [\sigma^2 F_o^2 + (A \cdot P)^2 + B \cdot P]$ ,  $P = (F_o^2 + 2F_c^2) / 3$ ;  $A$  and  $B$  are weight coefficients.

**DFT Calculations:** The electronic structures of CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) compounds, including their density of states (DOS) and electronic band structures, were calculated using Vienna Ab-initio Simulation Package.<sup>49-52</sup> The Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA)<sup>53</sup> was adopted to calculate the exchange-correlation potential, with an energy cutoff of 400 eV. The numerical integration of the Brillouin

zone was performed using a Monkhorst–Pack k-point sampling.<sup>54</sup> For CeBrMoO<sub>4</sub>, CeBrWO<sub>4</sub>, and CeClMoO<sub>4</sub>, the k-point mesh is  $5 \times 9 \times 7$ . For CeClWO<sub>4</sub>, with a larger unit cell, the k-point mesh is  $3 \times 7 \times 5$ . Pseudopotentials generated with the projector augmented-wave (PAW) method were employed.<sup>55</sup> To treat the highly correlated Ce 4f electrons, an on-site repulsion Hubbard parameter,  $U = 4$  eV, was used.<sup>56</sup>

**Photocurrent response measurement.** Crystals of CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) are very stable in air. Hence, crystals of CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) were manually crushed and grounded in mortar in air. Ethanol was employed to aid in forming suspension solutions. The suspension solution was slowly dropped on the ITO glass to form a uniform film. The uniformness of the prepared films was checked by an optical microscope. The films were dried at 393K under vacuum for 2 hours. The photocurrent performance of the photoanode was evaluated in a traditional three-electrode configuration, consisting of CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) photoanodes as the working electrode, platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. 1M Na<sub>2</sub>SO<sub>4</sub> aqueous solution was used as the electrolyte. Linear sweep voltammetry and I-t scans were collected on the electrochemical workstation (Gamry Interface 5000) under illumination of AM 1.5 (1 sun, 100 mW/cm<sup>2</sup>) using a solar simulator (Newport).

## Results and discussions

### Crystal growth and phase purification

Prior to this work, CeClMoO<sub>4</sub><sup>57-59</sup> and CeBrMoO<sub>4</sub><sup>60</sup> were reported. The high temperature solid-state method was employed to grow the crystals of CeClMoO<sub>4</sub><sup>57-59</sup> and CeBrMoO<sub>4</sub><sup>60</sup>. CeClMoO<sub>4</sub><sup>60</sup> was found as a phase-pure sample while significant amounts of impurity existed in CeBrMoO<sub>4</sub><sup>60</sup> samples. The previous work did not address crystal growth. In this work, we employed salt flux pairs of CeCl<sub>3</sub>/NaCl and CeBr<sub>3</sub>/NaBr to grow CeClMoO<sub>4</sub> and CeBrMoO<sub>4</sub>, respectively. Millimeter-sized crystals of CeClMoO<sub>4</sub> and CeBrMoO<sub>4</sub> were collected after salt flux was removed by DI water as shown in **Figure S1**. The phase purity of CeClMoO<sub>4</sub> and CeBrMoO<sub>4</sub> was verified by PXRD as shown in **Figure S2** and **Figure S3**, respectively. Two new tungsten-contained compounds, CeClWO<sub>4</sub> and CeBrWO<sub>4</sub>, were grown by salt flux as single-phase large crystals (**Figures S1, S4, and S5**). A combination of various halides would be a good flux for the crystal growth of oxyhalides<sup>32</sup>.

## Crystal Structure

CeHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) belongs to the REHaVIO<sub>4</sub> (RE=Y, La-Lu, Ha=Cl, Br; VI=Mo, W) family<sup>57-65</sup>, which exhibits abundant structural chemistry (*vide infra*). Two structure types were found within CeHaVIO<sub>4</sub> compounds. CeClMoO<sub>4</sub> is isostructural to CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub>. CeClWO<sub>4</sub> crystallizes in its own structure type. CeClMoO<sub>4</sub> was reported by Dorhout, P.K. et al in 2010, which crystallizes in centrosymmetric monoclinic space group  $P2_1/c$  (no. 14) with unit cell parameters of  $a = 19.1228(18)$  Å,  $b = 5.7992(5)$  Å, and  $c = 7.9591(7)$  Å, and  $\beta = 90.037(6)^\circ$ <sup>57</sup>. Our single crystal X-ray diffraction indicated that CeClMoO<sub>4</sub> forms in the acentric monoclinic space group  $Pc$  (no. 7) with unit cell parameters of  $a = 9.5513(1)$  Å,  $b = 5.793(1)$  Å, and  $c = 7.9495(1)$  Å, and  $\beta = 90.014(1)^\circ$ , which was also verified by SHG measurements (*vide infra*). CeBrMoO<sub>4</sub> is isostructural to CeClMoO<sub>4</sub>, which was confirmed by our experimental results and a previous study<sup>60</sup>. CeBrWO<sub>4</sub> is a new compound, which was never reported. Like CeBrMoO<sub>4</sub> and CeClMoO<sub>4</sub>, CeBrWO<sub>4</sub> is also isotypic to LaBrWO<sub>4</sub><sup>32</sup> and crystallizes in the acentric monoclinic space group  $Pc$  (no.7) with unit cell parameters of  $a = 9.8783(1)$  Å,  $b = 5.9223(1)$  Å, and  $c = 7.9394(1)$  Å, and  $\beta = 90.008(1)^\circ$ .

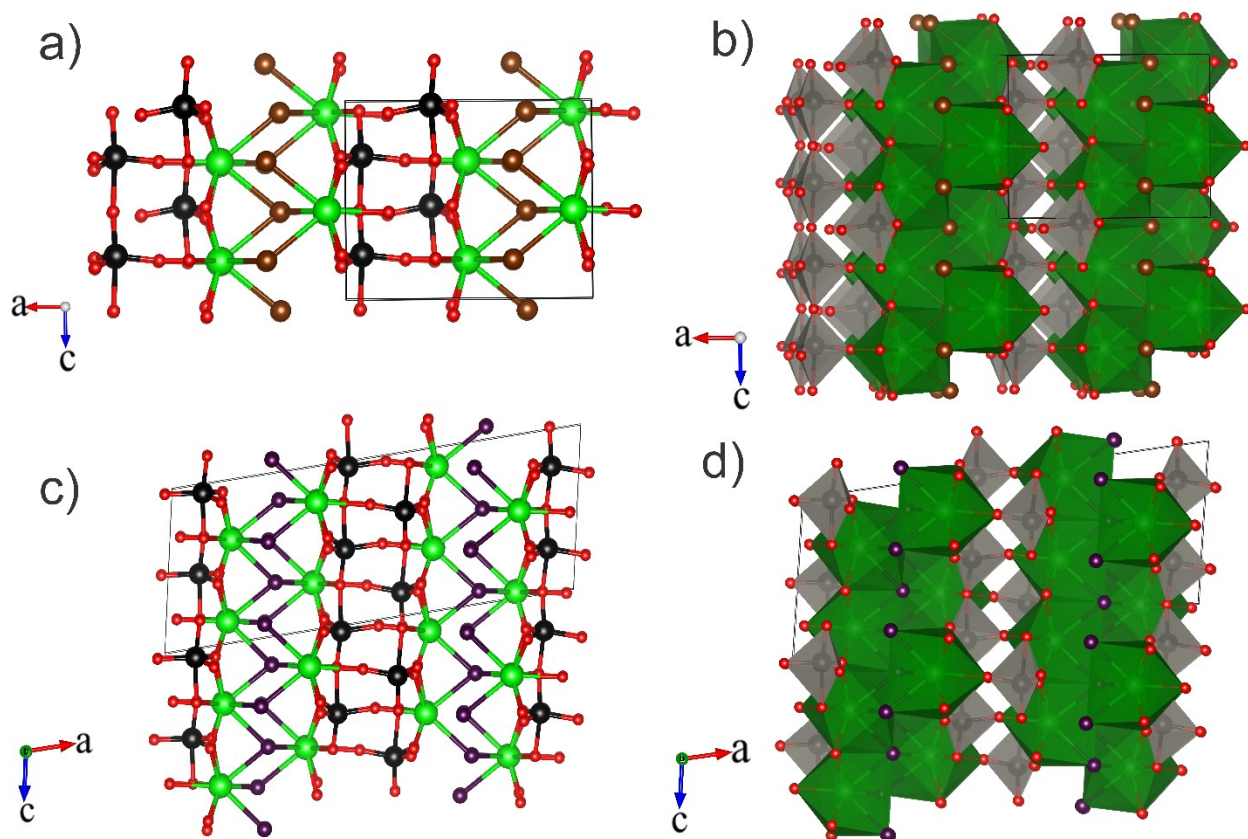
The  $\beta$  angles of all these structures are very close to  $90^\circ$ , making them pseudo-orthorhombic. However, orthorhombic symmetry was precluded because we tested orthorhombic space groups and they all result in much higher R-values and significant residual electron peaks and holes. Due to the pseudo-orthorhombic acentric symmetry, the twinning laws for inversion and  $180^\circ$  rotation along  $a$ -axis were both considered in our structural refinement.

To simplify the discussion, CeBrWO<sub>4</sub> is selected to present the structure of CeBrMoO<sub>4</sub> and CeClMoO<sub>4</sub>. The Wyckoff sequence of CeBrWO<sub>4</sub> is  $a^{14}$  with the Pearson symbol  $mP28$ . There are two distinct Ce atoms, two distinct W atoms, two distinct Br atoms, and eight distinct O atoms in the asymmetric unit cell of CeBrWO<sub>4</sub> with full occupancy. The crystal structure of CeBrWO<sub>4</sub> is summarized in **Figures 1a and 1b**. CeBrWO<sub>4</sub> forms a three-dimensional (3D) framework, which is constructed by two-dimensional (2D) [CeBrO<sub>4</sub>]<sup>6-</sup> strips and one-dimensional (1D) [WO<sub>5</sub>] strands. The 1D [WO<sub>5</sub>] strands are constructed by distorted [WO<sub>5</sub>] trigonal bipyramids, which connect to each other via apical oxygen atoms and run along the [001] direction. Five oxygen atoms surround central W atoms with four short interactions of 1.755(7) - 1.842(6) Å and one long

interaction of 2.230(5)-2.239(5) Å. Our previous bonding picture study of LaBrWO<sub>4</sub> revealed the moderately strong interaction of the elongated W-O interactions of 2.24 Å<sup>32</sup>. The 2D [CeBrO<sub>4</sub>]<sup>6-</sup> strips are built by distorted tetracapped trigonal prisms [CeO<sub>6</sub>Br<sub>3</sub>], where six oxygen atoms and three bromine atoms surround the central Ce atoms. The Ce-Br interactions fall into the range of 3.1393(16) - 3.257(2) Å, which is similar to many compounds that include Ce-Br interactions such as, CeBr<sub>3</sub> (3.108-3.158 Å)<sup>66</sup>, CeBrMoO<sub>4</sub> (3.112-3.227 Å)<sup>60</sup>, Ce<sub>3</sub>(SiS<sub>4</sub>)<sub>2</sub>Br (3.101-3.328 Å)<sup>67</sup>, etc. The Ce-O interactions are within the range of 2.473(8)-2.697(9) Å of CeBrWO<sub>4</sub>, which are comparable to many oxides such as K<sub>6</sub>Ce<sub>2</sub>(SO<sub>4</sub>)<sub>6</sub> (2.498-2.648 Å)<sup>68</sup>, CeBrMoO<sub>4</sub> (2.466-2.726 Å)<sup>60</sup>, CeCu<sub>3</sub>Co<sub>4</sub>O<sub>12</sub> (2.486 Å)<sup>69</sup>, CeMoBO<sub>6</sub> (2.427-2.619 Å)<sup>70</sup>, etc.

CeClWO<sub>4</sub> is a new compound, which crystallizes in a new structure type. CeClWO<sub>4</sub> adopts a different unit cell:  $a = 19.6059(2)$  Å,  $b = 5.89450(10)$  Å, and  $c = 7.80090(10)$  Å, and  $\beta = 101.4746(8)^\circ$ , which is a 2 $\times$  supercell structure of the other three title compounds with the transformation matrix being (2 0 ½, 0 1 0, 0 0 1). This can be demonstrated by comparing the ( $h1l$ ) reciprocal lattice planes (**Figure S6**). The refined structure is also in the acentric monoclinic  $Pc$  (no. 7) space group. The details of refinement are included in **Table 1**. The acentric structure nature of CeClWO<sub>4</sub> was also verified by second harmonic generation measurements (*vide infra*). Interestingly, our refined unit cell parameters of CeClWO<sub>4</sub> are comparable to those of the  $P2_1/c$  CeClMoO<sub>4</sub> structure reported by Dorhout, except for the  $\beta$  angle (101.5° vs 90.0°).<sup>57</sup> The Wyckoff sequence of CeClWO<sub>4</sub> is  $a^{28}$  with the Pearson symbol  $mP56$ . There are four distinct Ce atoms, four distinct W atoms, four distinct Cl atoms, and sixteen distinct O atoms in the asymmetric unit cell of CeClWO<sub>4</sub> with full occupancy. The crystal structure of CeClWO<sub>4</sub> is exhibited in **Figures 1b** and **1c**. The 3D crystal structure of CeClWO<sub>4</sub> is similar to 3D CeBrWO<sub>4</sub> with doubling the [100] axis. The 3D framework of CeClWO<sub>4</sub> is constructed by 2D [CeClO<sub>4</sub>]<sup>6-</sup> strips and 1D [WO<sub>5</sub>] strands. The 2D [CeClO<sub>4</sub>]<sup>6-</sup> strips are made by distorted tetracapped trigonal prisms [CeO<sub>6</sub>Cl<sub>3</sub>] via sharing vertices and edges. The 1D [WO<sub>5</sub>] strands within CeClWO<sub>4</sub> are constructed by distorted [WO<sub>5</sub>] trigonal bipyramids, which were also found within CeBrWO<sub>4</sub>. The W-O interactions within CeClWO<sub>4</sub> are 1.730(9) Å-2.190(9) Å, which is comparable with W-O interactions of CeBrWO<sub>4</sub> (1.755(7) Å - 2.239(5) Å).



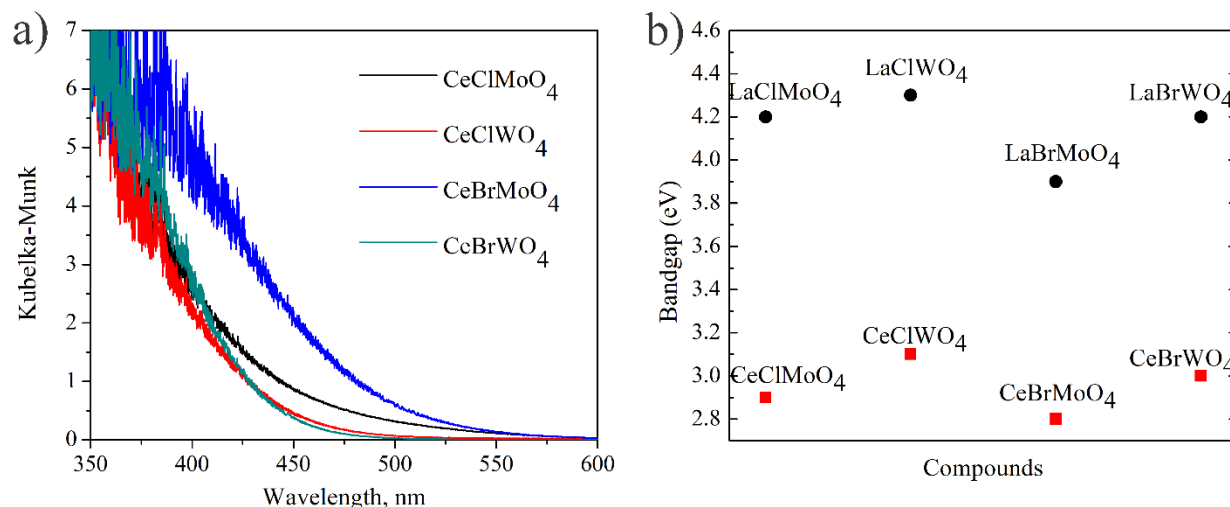


**Figure 1.** (a) Ball-stick structure and (b) polyhedral structure of  $\text{CeBrWO}_4$  viewed along the  $[010]$  direction. (c) Ball-stick structure and (d) polyhedral structure of  $\text{CeClWO}_4$  viewed along the  $[010]$  direction. Ce: green, W: black, O: red, Br: brown, and Cl: purple.

$\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ , La-Lu,  $\text{Ha}=\text{Cl}$ , Br;  $\text{VI}=\text{Mo}$ , W) family exhibits very rich structure chemistry. Prior to this work, seven structure types were reported for the  $\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ , La-Lu,  $\text{Ha}=\text{Cl}$ , Br;  $\text{VI}=\text{Mo}$ , W) family, which is summarized in **Table S3**<sup>57-65</sup>. The comparison of physical properties such as magnetic properties, bandgaps, and photoluminescent properties between  $\text{CeHaVIO}_4$  and the compounds of  $\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ , La-Lu,  $\text{Ha}=\text{Cl}$ , Br;  $\text{VI}=\text{Mo}$ , W) family were summarized in Table S3. This work of  $\text{CeClWO}_4$  adds the eighth structure type to the  $\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ , La-Lu,  $\text{Ha}=\text{Cl}$ , Br;  $\text{VI}=\text{Mo}$ , W) family. Compared to their differences, these structures exhibit more similarity. 3D framework structure constructed by  $[\text{REO}_x\text{Ha}_y]$  polyhedra and  $[\text{VIO}_z]_{z=4 \text{ or } 5}$  units is a common feature for the  $\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ , La-Lu,  $\text{Ha}=\text{Cl}$ , Br;  $\text{VI}=\text{Mo}$ , W) family. The 1D  $[\text{VIO}_5]_{\text{VI}=\text{Mo or W}}$  strands were also discovered within  $\text{CeClMoO}_4$  (space group  $P2_1/c$ ) structure type<sup>57</sup>,  $\text{LaClWO}_4$  (space group  $Pbc2_1$ ) structure type<sup>61</sup>, and  $\text{LaClWO}_4$  (space group  $Pmcn$ ) structure type<sup>61</sup>. The discrepancies between structures reported for the same

compound, such as Dorhout's  $\text{CeClMoO}_4$  in  $P2_1/c$  vs. this work's  $\text{CeClMoO}_4$  in  $Pc$ , is likely due to polymorphism – a given  $\text{REHaVIO}_4$  compound may adopt similar but different crystal structures, especially when prepared with different synthetic methods. For example,  $\text{LaClWO}_4$  crystallizes in acentric orthorhombic  $\text{Pbc}2_1$  and centrosymmetric orthorhombic  $\text{Pmcn}$  space group<sup>60</sup>. In our own study of  $\text{LaHaVIO}_4$  and  $\text{CeHaVIO}_4$ , we found crystals whose diffraction patterns indicate much larger unit cells or even exhibit diffused scattering, which suggests the possible intergrowth between different polymorph structures. We are devoting more efforts into these challenging crystals in hope to provide more insights into the abundant structural chemistry in the  $\text{REHaVIO}_4$  ( $\text{RE}=\text{Y}$ ,  $\text{La-Lu}$ ,  $\text{Ha}=\text{Cl}$ ,  $\text{Br}$ ;  $\text{VI}=\text{Mo}$ ,  $\text{W}$ ) family, which accounts for their broad applications such as photoluminescent applications,<sup>62</sup> NLO applications,<sup>32</sup> and the photocurrent response in this work.

### Linear Optical properties



**Figure 2.** (a) Kubelka-Munk diffuse reflectance solid-state UV-Vis spectra of  $\text{CeHaVIO}_4$  ( $\text{Ha}=\text{Cl}$ ,  $\text{Br}$ ;  $\text{VI}=\text{Mo}$ ,  $\text{W}$ ). (b) The comparison of bandgaps between  $\text{CeHaVIO}_4$  ( $\text{Ha}=\text{Cl}$ ,  $\text{Br}$ ;  $\text{VI}=\text{Mo}$ ,  $\text{W}$ ) and  $\text{LaHaVIO}_4$  ( $\text{Ha}=\text{Cl}$ ,  $\text{Br}$ ;  $\text{VI}=\text{Mo}$ ,  $\text{W}$ ) compounds.

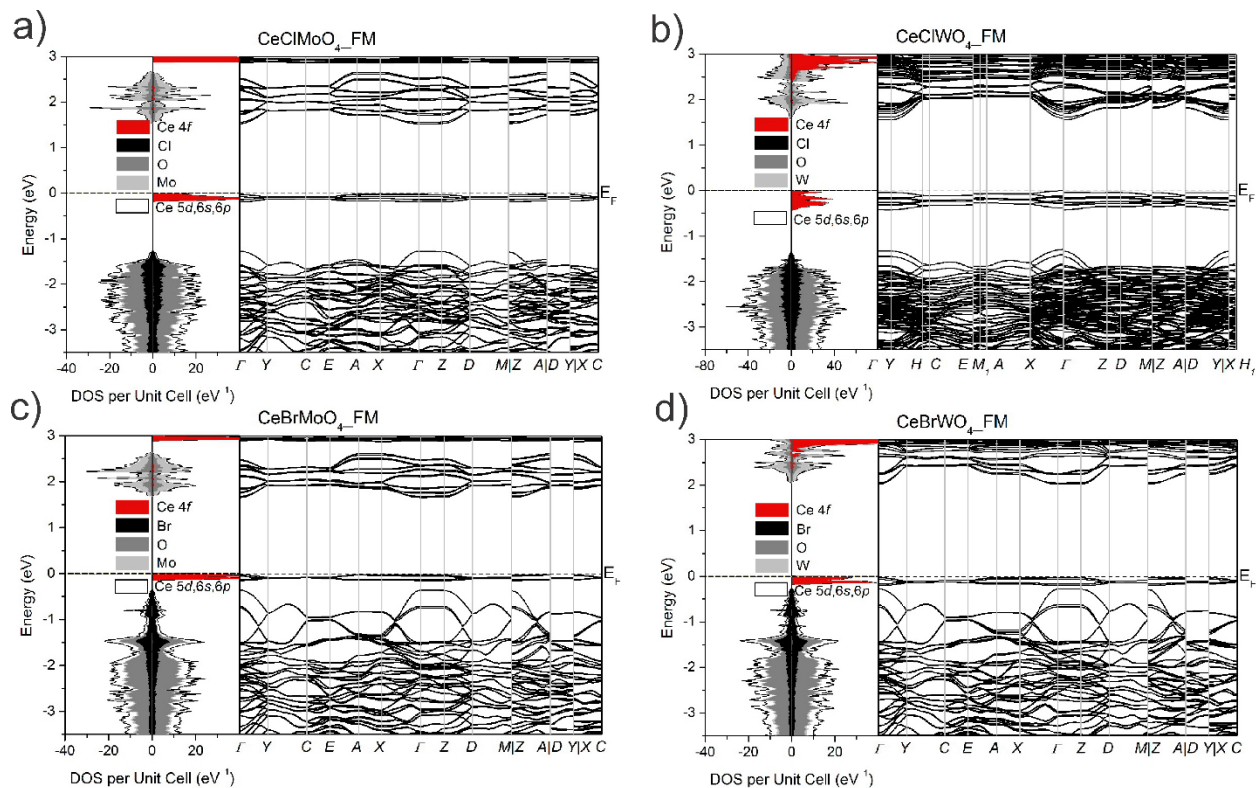
The optical bandgaps of  $\text{CeHaVIO}_4$  ( $\text{Ha}=\text{Cl}$ ,  $\text{Br}$ ;  $\text{VI}=\text{Mo}$ ,  $\text{W}$ ) were estimated by UV-Vis spectrum measurements (**Figure 2a**).  $\text{CeClWO}_4$  is similar to  $\text{CeBrWO}_4$ , which exhibits a transition around 450nm. Based on electronic structure calculation,  $\text{CeHaVIO}_4$  are direct-bandgap semiconductors (*vide infra*). The direct allowed transitions of  $\text{CeHaVIO}_4$  were calculated by the Tauc plots, which were shown in **Figure 2b**. The calculated direct bandgap of  $\text{CeClWO}_4$  and  $\text{CeBrWO}_4$  are 3.1(1)

eV and 3.0(1) eV, respectively. There is a transition around 500 nm observed for CeClMoO<sub>4</sub>, which results in the calculated direct bandgap of 2.9(1) eV. The CeBrMoO<sub>4</sub> possesses the smallest bandgap of 2.8(1) eV, which originates from its transition around 575 nm. Compared with the isostructural counterparts LaHaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W), the bandgaps of CeHaVIO<sub>4</sub> compounds are much smaller (**Figure 2b**). The suppression of bandgaps of CeHaVIO<sub>4</sub> compounds originate from the partially filled *4f* orbitals of Ce atoms (*vide infra*). The bandgap suppression also agreed well with the physical appearance of crystals of REHaVIO<sub>4</sub> (RE=La, Ce; Ha=Cl, Br; VI=Mo, W), where LaHaVIO<sub>4</sub> and CeHaVIO<sub>4</sub> compounds are colorless and colorful <sup>32</sup>, respectively. Tuning the bandgap of inorganic solids is crucial for many applications such as second harmonic generation <sup>25</sup> and photovoltaics <sup>71</sup>. Our attempts to tune the bandgap of CeHaVIO<sub>4</sub> via replacing Ce with La was found to be effective. As shown in **Figures S7-S10**, (La<sub>0.5</sub>Ce<sub>0.5</sub>)ClMoO<sub>4</sub>, (La<sub>0.5</sub>Ce<sub>0.5</sub>)ClWO<sub>4</sub>, (La<sub>0.5</sub>Ce<sub>0.5</sub>)BrMoO<sub>4</sub>, and (La<sub>0.5</sub>Ce<sub>0.5</sub>)BrWO<sub>4</sub> were found to be single phase samples. The bandgap of (La<sub>0.5</sub>Ce<sub>0.5</sub>) ClMoO<sub>4</sub>, (La<sub>0.5</sub>Ce<sub>0.5</sub>)ClWO<sub>4</sub>, (La<sub>0.5</sub>Ce<sub>0.5</sub>)BrMoO<sub>4</sub>, and (La<sub>0.5</sub>Ce<sub>0.5</sub>)BrWO<sub>4</sub> were estimated by UV-Vis measurements to be 3.8(1) eV, 3.5(1) eV, 3.6(1) eV, and 3.9(1) eV, respectively. As shown in **Figure S11**, the bandgap of (La<sub>0.5</sub>Ce<sub>0.5</sub>)HaVIO<sub>4</sub> (Ha=Cl, Br; VI=Mo, W) samples reside between CeHaVIO<sub>4</sub> and LaHaVIO<sub>4</sub> samples. Mixing La and Ce would be a good strategy to tune their bandgaps. The narrowed bandgaps of CeHaVIO<sub>4</sub> compounds result in good transmission in the IR range. The infrared spectrum of CeHaVIO<sub>4</sub> compounds are shown in **Figures S12 and S13**. There were no intrinsic vibrational absorption chemical bonds in the wavelength of 2.5–18.2 μm for all CeHaVIO<sub>4</sub> compounds. CeClWO<sub>4</sub> and CeBrWO<sub>4</sub> exhibited comparable IR spectra with three absorption peaks detected around 550 cm<sup>-1</sup>, which agree well with LaBrWO<sub>4</sub> <sup>32</sup>. The strong absorption peaks around 550 cm<sup>-1</sup> can be assigned to the ν(W-O) vibrations <sup>32</sup>. The IR spectrum of CeClMoO<sub>4</sub> is comparable to CeBrMoO<sub>4</sub> with two strong absorption peaks detected around 550 cm<sup>-1</sup>, which originate from the ν(Mo-O) vibrations <sup>32</sup>. A comparable IR spectrum was also found in LaBrMoO<sub>4</sub> <sup>32</sup>.

## Electronic Structures

LaHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) is isostructural to CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W), except CeClWO<sub>4</sub>. It would be interesting to investigate why there are significant bandgap differences

between them. Hence, we employed DFT calculations to study the electronic structures of CeHaVIO<sub>4</sub> (**Figures 3, S14-S18**).



**Figure 3.** The DOS curves and electronic band structures of CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W).

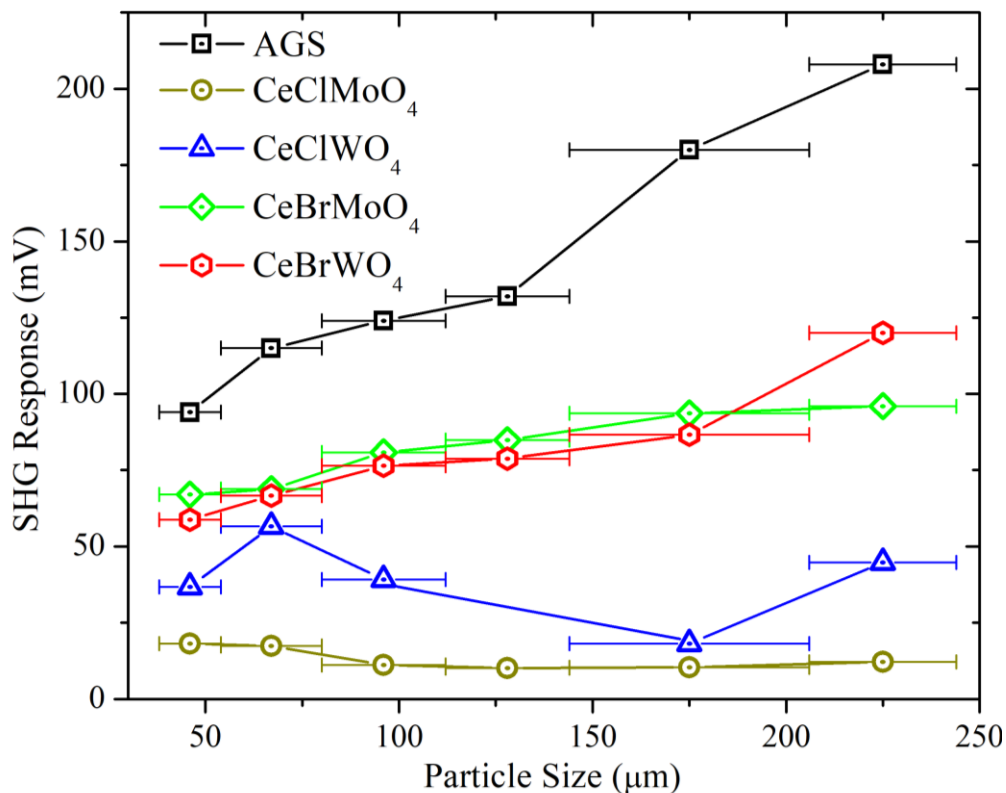
Using the structures from single crystal refinement, we calculated the DOS and electronic band structures of CeClMoO<sub>4</sub>, CeClWO<sub>4</sub>, CeBrMoO<sub>4</sub>, and CeBrWO<sub>4</sub>. Due to the strong correlation of Ce 4*f* electrons, the Hubbard parameter ( $U = 4$  eV) had to be employed. Otherwise, the self-consistent calculations do not converge. Formally, the valence of Ce is +3, which means each Ce atom has one 4*f* electron and thus 1  $\mu_B$  local moment. Because there are multiple Ce atoms in a unit cell, we tried both ferromagnetic and antiferromagnetic ordering of Ce atoms' local moments as well. **Figure 3** lists the DOS and band structures from ferromagnetic calculations of the four compounds. The antiferromagnetic results are shown in **Figure S15-18** in Supporting Information. From both sets of results, we can draw the same conclusions below.

The most prominent feature among all these CeHaVIO<sub>4</sub> compounds is their highly localized Ce 4*f* states. They form a narrow peak in the DOS and very flat bands in the band structures. Moreover, it represents the valence band edges in all cases. For comparison, we also calculated the electronic

structure for LaBrWO<sub>4</sub>, which is also shown in **Figure S14**. La has no 4f electron in LaHaVIO<sub>4</sub>. As a result, the La 4f states are absent in DOS and band structure. The valence band edge is mainly contributed by Br states. This comparison clearly explains the band gap differences between CeHaVIO<sub>4</sub> and LaHaVIO<sub>4</sub> – Ce's 4f states significantly reduce the band gap of CeHaVIO<sub>4</sub>. The calculated bandgaps for CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) are around 2 eV, which are smaller than experimentally estimated values. The underestimation of bandgaps of inorganic solids is common for DFT calculations<sup>72</sup>. DFT calculations confirmed the semiconducting nature of CeHaVIO<sub>4</sub>, which was also verified by UV-Vis measurements. The charge-balanced formula (Ce<sup>3+</sup>)(Ha<sup>-</sup>)(VI<sup>6+</sup>)(O<sup>2-</sup>)<sub>4</sub> can be established by assigning a formal charge of 3+ to the Ce atoms, 6+ to the Mo and W atoms, 1- to the Cl and Br atoms, and 2- to the O atoms. Bond valence sum calculations found the BVS of Ce atoms and W atoms to be 2.98 and 5.95 receptivity for CeClWO<sub>4</sub>, which suggests Ce atoms and W atoms with oxidation 3+ and 6+, respectively<sup>24</sup>.

### Nonlinear Optical properties

The nonlinear optical properties of CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) were measured and presented in **Figure 4**. All samples exhibited SHG response under 2090 nm incident lasers, which confirmed the acentric nature of CeHaVIO<sub>4</sub> samples. CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> own comparable SHG responses of 0.58× AGS and 0.46× AGS, respectively for samples of 225 μm particle. The SHG intensity of CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> increases with increasing particle size, which indicates that CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> are type-I phase-matching materials. CeClWO<sub>4</sub> exhibited a much lower SHG response of 0.22× AGS for a sample of 225 μm particle. CeClMoO<sub>4</sub> possessed the lowest SHG response of 0.06× AGS for samples of 225 μm particle. CeClMoO<sub>4</sub> and CeClWO<sub>4</sub> are not type-I phase-matching materials, and the SHG intensity of CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> decreases as the particle size increases (**Figure 4**). The isostructural nature and comparable bandgaps between CeBrMoO<sub>4</sub>, CeBrWO<sub>4</sub>, and CeClMoO<sub>4</sub> result in distinct SHG responses. CeClMoO<sub>4</sub> and CeClWO<sub>4</sub> are non-phase-matching materials compared to CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub>. Many factors such as the crystal quality or different crystal structures would significantly affect NLO properties<sup>73</sup>. The future planned study will be focused on measurements of the birefringence of CeHaVIO<sub>4</sub> to understand this difference. The higher degree distortion of 1D [VIO<sub>5</sub>]<sub>VI=Mo or W</sub> strands plays an important role in enhancing SHG within CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub>, which was also observed for LaBrWO<sub>4</sub> compared to LaBrMoO<sub>4</sub><sup>32</sup>.



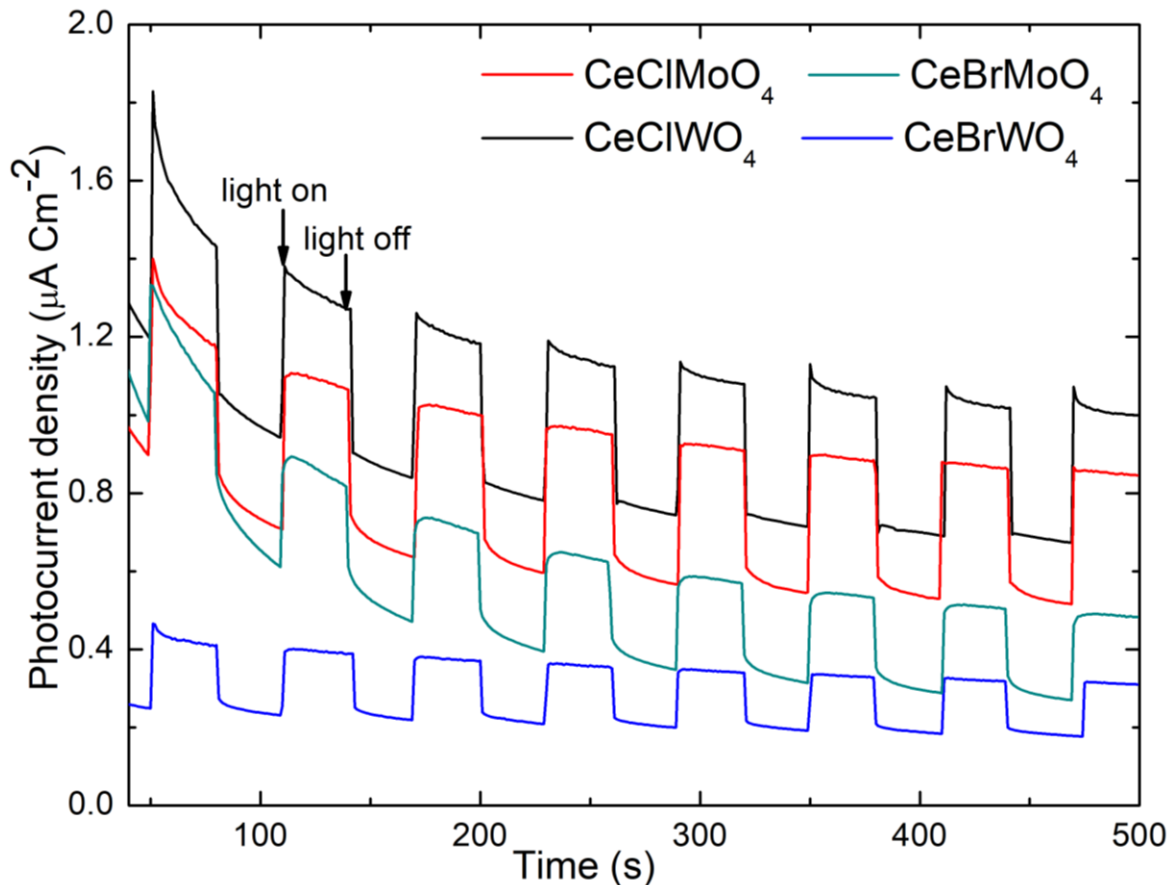
**Figure 4.** Size-dependent SHG intensities of CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) samples and the AgGaS<sub>2</sub> (AGS) reference.

### Photocurrent response

The bandgaps of CeHaVIO<sub>4</sub> fall into the range of 2.8(1)-3.1(1) eV, which originates from the presence of partially filled 4*f* orbitals of cerium. These partially filled 4*f* orbitals populate between the valance band and conduction band. CeHaVIO<sub>4</sub> crystals can absorb visible light due to their small bandgap nature (**Figure 2a**). The capability of absorption of visible lights coupled with excellent ambient stability contributed to us exploring the photocurrent response of CeHaVIO<sub>4</sub> samples. A material that can generate high photocurrent density under light radiation can be used for photovoltaics to reduce our dependence on fossil energy<sup>24, 28</sup>. The photocurrent response of CeHaVIO<sub>4</sub> samples are presented in **Figure 5**. As shown in **Figure 5**, CeHaVIO<sub>4</sub> samples exhibit good photocurrent response. The reproducibility of the photocurrent response of CeHaVIO<sub>4</sub> samples were tested by measuring three samples of each specimen, which are summarized in **Figures S19-S22**. All CeHaVIO<sub>4</sub> samples exhibited good reproducibility. CeClMoO<sub>4</sub> and CeClWO<sub>4</sub> exhibited comparable photocurrent responses of 332 nA Cm<sup>-2</sup> and 369 nA Cm<sup>-2</sup>,

respectively. The photocurrent density of CeBrMoO<sub>4</sub> was 263 nA Cm<sup>-2</sup>. CeBrWO<sub>4</sub> possessed the lowest photocurrent response of 138 nA Cm<sup>-2</sup>. The photocurrents of CeHaVIO<sub>4</sub> samples slightly decrease after a few cycles, which was observed in many photocurrent-responding materials and originates from the photocorrosion of photoanodes<sup>24, 28</sup>. A comparison of photocurrent response among CeHaVIO<sub>4</sub> and many previously reported sulfides and oxyhalides are tabulated in **Table S4**<sup>74-89</sup>. CeHaVIO<sub>4</sub> exhibit comparable or better photocurrent response than many compounds such as Eu<sub>3</sub>Gd<sub>6</sub>MgS<sub>2</sub>B<sub>20</sub>O<sub>41</sub> (0.12 μA/cm<sup>2</sup>)<sup>78</sup>, Sr<sub>6</sub>Cd<sub>2</sub>Sb<sub>6</sub>S<sub>10</sub>O<sub>7</sub> (0.065μA/cm<sup>2</sup>)<sup>77</sup>, BaCuSbS<sub>3</sub> (0.055 μA/cm<sup>2</sup>)<sup>76</sup>, BaCuSbSe<sub>3</sub> (0.03μA/cm<sup>2</sup>)<sup>76</sup>, RbIn<sub>4</sub>S<sub>6</sub>Cl (0.029μA/cm<sup>2</sup>)<sup>75</sup>, Pb<sub>5</sub>Sn<sub>3</sub>S<sub>10</sub>Cl<sub>2</sub> (0.019μA/cm<sup>2</sup>)<sup>75</sup>, Rb<sub>2</sub>Ba<sub>3</sub>Cu<sub>2</sub>Sb<sub>2</sub>S<sub>10</sub> (0.006μA/cm<sup>2</sup>)<sup>74</sup>. Photocurrent measurements can be useful to extract more intrinsic properties of inorganic solids. An external quantum efficiency (EQE) measurement can be employed to determine the bandgaps of CeHaVIO<sub>4</sub><sup>90</sup>, which are undergoing. CeHaVIO<sub>4</sub> system exhibits both good NLO properties and photocurrent response, which indicates that they are good multifunctional materials. There might exist more new compounds in the REHaVIO<sub>4</sub>(RE=La-Lu, Ha=Cl, Br, VI=Mo, W) system, which may uncover more multifunctional materials. The discovery of new heteroanionic compounds usually results in exciting physical properties such as recent works of C(NH<sub>2</sub>)<sub>3</sub>BF<sub>4</sub><sup>91</sup> and Ca<sub>2</sub>B<sub>3</sub>O<sub>6</sub>X (X = Cl and Br)<sup>92</sup>.





**Figure 5.** Photocurrent density of CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) photoanodes over time.

## Conclusions

Millimeter-sized crystals of four heteroanionic oxyhalides, CeClMoO<sub>4</sub>, CeBrMoO<sub>4</sub>, CeClWO<sub>4</sub>, and CeBrWO<sub>4</sub>, had been grown by a halide salt flux method, which are stable in ambient air for a long time. CeClMoO<sub>4</sub>, CeBrMoO<sub>4</sub>, CeClWO<sub>4</sub>, and CeBrWO<sub>4</sub> were studied as multifunctional materials, which combine good second harmonic generation (SHG) response and photocurrent signals. Two structure types were found for the CeHaVIO<sub>4</sub> (Ha=Cl, Br, VI=Mo, W) system. CeClMoO<sub>4</sub> is isostructural to CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub>, which forms in the LaBrMoO<sub>4</sub> structure type. CeClWO<sub>4</sub> crystallizes in a new structure type, which adds the eighth structure type to the REHaVIO<sub>4</sub> (RE=Y, La-Lu, Ha=Cl, Br; VI=Mo, W) family. The CeHaVIO<sub>4</sub> system features a 3D framework, which is made by 2D [REHaO<sub>4</sub>]<sup>6-</sup> strips and 1D [VIO<sub>5</sub>] strands. Compared with isostructural LaHaVIO<sub>4</sub> system, the bandgaps of CeHaVIO<sub>4</sub> system are significantly suppressed from 3.9(1)-4.3(1) eV to 2.8(1)-3.1(1) eV, respectively. The presence of partially filled 4*f* orbitals



of cerium atoms accounts for the narrower bandgaps of CeHaVIO<sub>4</sub>. The CeHaVIO<sub>4</sub> system all exhibited SHG responses. CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> are both type-I phase-matching materials, which possess moderate SHG response of 0.58× and 0.46× AGS, respectively. CeBrMoO<sub>4</sub> and CeBrWO<sub>4</sub> are good candidates for IR NLO application due to their moderate SHG response, easy-growth of crystals, high ambient stability, and type-I phase-matching behavior. CeHaVIO<sub>4</sub> films can also generate photocurrent response in the range of 138 nA Cm<sup>-2</sup>- 369 nA Cm<sup>-2</sup> upon light radiation. The REHaVIO<sub>4</sub> (RE=Y, La-Lu, Ha=Cl, Br; VI=Mo, W) family owns rich structural chemistry, which has eight structure types. Functionalities such as NLO application, photoluminescent response, and photocurrent response were found within the REHaVIO<sub>4</sub> family, where more multifunctional materials can be grown by halide salt flux methods.

## **ASSOCIATED CONTENTS**

### **Supporting Information**

The refined crystallographic data, crystal structure summary of the REHaVIO<sub>4</sub> (Ha=Cl, Br; RE=La-Lu; VI=Mo, W) system, comparison of photocurrent density, microscope photos of crystals, lab powder X-ray diffraction results, the (h1l) planes, IR spectrum, DOS plots, photocurrent density results.

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## Notes

The authors declare no competing financial interest.

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