SPECIAL TOPIC: Dedicated to the 70th Birthday of Professor Kenneth R. Poeppelmeier

Designing excellent mid-infrared nonlinear optical materials with fluorooxo-functional group of d^0 transition metal oxyfluorides

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ABSTRACT Exploration of new infrared (IR) nonlinear optical (NLO) materials is still in urgency owing to the indispensable roles in optoelectronic devices, resource exploration, and long-distance laser communication. The formidable challenge is to balance the contradiction between wide band gaps and large second harmonic generation (SHG) effects in IR NLO materials. In the present work, we proposed new kinds of NLO active units, d^0 transition metal fluorooxo-functional groups for designing mid-IR NLO materials. By studying a series of d^0 transition metal oxyfluorides (TMOFs), the influences of fluorooxo-functional groups with different d^0 configuration cations on the band gap and SHG responses were explored. The results reveal that the fluorooxo-functional groups with different d^0 configuration cations can enlarge band gaps in mid-IR NLO materials. The first-principles calculations demonstrate that the nine alkali/alkaline earth metals d^0 TMOFs exhibit wide band gaps (all the band gaps > 3.0 eV), large birefringence Δn (> 0.07), and two W/Mo TMOFs also exhibit large SHG responses. Moreover, by comparing with other fluorooxo-functional groups, it is found that introducing fluorine into building units is an effective way to enhance optical performance. These d^0 TMOFs with superior fluorooxo-functional groups represent a new exploration family of the mid-IR region, which sheds light on the design of mid-IR NLO materials possessing large band gap.

Keywords: infrared nonlinear optical materials, second harmonic generation, d^0 transition metal oxyfluorides, fluorooxo-functional groups

INTRODUCTION

Nonlinear optical (NLO) materials exert a crucial role in

the pursuit of coherent light producing lasers which are extensively used in optical communication and industry [1–10]. From the infrared (IR) to ultraviolet (UV)/deep-UV (DUV) region, some typical materials are employed, such as $\text{KBe}_2\text{BO}_3\text{F}_2$ [11], $\beta\text{-BaB}_2\text{O}_4$ [12], LiB_3O_5 [13], KH_2PO_4 [14], KTiOPO_4 [15], AgGaQ_2 ($\text{Q} = \text{S}, \text{Se}$) [16] and ZnGeP_2 [17]. However, commercially available IR NLO materials AgGaS_2 and ZnGeP_2 hardly satisfy the demands of practical applications owing to low laser damage threshold (LDT) or two-photon absorption [18]. In this regard, it is still imperative to search alternative mid-IR NLO materials with wide band gap and strong second harmonic generation (SHG) effects.

In order to achieve NLO compounds with non-centrosymmetric structures, various advantageous functional building units are involved to generate large SHG intensities [19–28], which include (i) planar triangle anionic groups with conjugated π configurations such as $(\text{BO}_3)^{3-}$, $(\text{CO}_3)^{2-}$, $(\text{NO}_3)^-$, etc.; (ii) d^{10} transition-metal cations Hg^{2+} , Zn^{2+} and Cd^{2+} , etc. with polar displacement; (iii) Pb^{2+} , Sb^{3+} and Bi^{3+} cations with the stereochemically active lone pair (SCALP); (iv) functional building units $\text{BO}_x\text{F}_{4-x}$ ($x = 1, 2, 3$, [BOF]) in fluorooxoborates; (v) d^0 transition metal (d^0 TM) cations (Ti^{4+} , V^{5+} , Nb^{5+} , Ta^{5+} , Mo^{6+} and W^{6+}) with second-order Jahn-Teller (SOJT) distortions. These units or their derivatives can be incorporated to explore new NLO materials in UV/DUV or IR regions.

Meanwhile, the exploration of new mid-IR NLO materials with targeted properties remains urgent. The main challenge is how to balance the contradiction between

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wide band gaps ($E_g \geq 3.0$ eV) and large NLO susceptibilities ($d_{ij} \geq 10 \times \text{KH}_2\text{PO}_4$ (KDP, $d_{36} = 0.39$ pm/V)) in mid-IR materials. In order to ease this contradiction, metal chalcogenides [21,29–33], metal halides [34–36], metal oxides [37] and metal oxyhalides [38,39] have been explored systematically by computational or experimental methodology [29–40]. Introduction of fluorine with large electronegativity into NLO materials is an excellent route for ensuring wide band gap. Very recently, it has been proven that introducing fluorine into borates (fundamental building block (FBB): BO_3 , BO_4), phosphates (FBB: PO_4), silicates (FBB: SiO_4 , SiO_6) to form fluorooxo-functional groups is one of the effective ways to enhance the band gap and SHG response [41–44]. Compared with the $\text{BO}_4/\text{PO}_4/\text{SiO}_6$ FBBs, the fluorooxo-functional groups [BOF], $\text{PO}_x\text{F}_{4-x}$ ($x = 2, 3$, [POF]), $\text{SiO}_x\text{F}_{6-x}$ ($x = 1, 2, 3, 4, 5$, [SiOF]) exhibit large first order hyperpolarizability, which are conducive to enlarging the SHG performances of crystals [41–44]. Under this strategy, a series of outstanding UV fluorooxoborates were discovered, such as the $\text{NH}_4\text{B}_4\text{O}_6\text{F}$ family [28,45] and other fluorooxoborates [46,47]. On the other hand, d^0 TM cations with SOJT distortions can lead to strong SHG responses [48,49]. In that case, d^0 TM, oxygen and fluorine are introduced to form polyhedra in a crystal which exhibits geometrical distortion due to different interactions between d^0 TM–(O and F) (e.g., MoO_3F_3 , NbOF_5) bonds [50–53]. According to Pauling's second crystal rule, partial substitution of fluorine for oxygen can produce complicated crystal structures [54,55]. Considering the superiority of fluorine element in enlarging band gap and d^0 TM ability of SOJT effects in producing strong SHG intensities in NLO materials, we proposed a feasible strategy to introduce d^0 TM fluorooxo-functional groups to explore mid-IR materials.

To explore the groups that are beneficial to exploring mid-IR materials, in this work we focus on the d^0 transition metal oxyfluorides (d^0 TMOFs). There are 39 asymmetric d^0 TMOFs in the inorganic crystal structure database (ICSD, Version 4.2.0, build 20190819-1703), herein disordered compounds are excluded (listed in Table S1). Because alkali/alkaline earth metals enlarge band gap [33], we mainly discuss nine alkali/alkaline earth metals d^0 TMOFs, namely ATMOFs ($A = \text{IA}/\text{IIA}$ metals, $\text{TM} = \text{Ti}, \text{V}, \text{Nb}, \text{Ta}, \text{Mo}$ and W). In the nine ATMOFs, they all possess wide band gaps. This work demonstrates an alternative route to search for better candidate materials for high LDT performances in mid-IR NLO crystals.

THEORETICAL CALCULATIONS

First-principles calculations were performed by the plane-wave pseudo-potential method implemented in the CASTEP package [56]. Band structures and optical properties were calculated *via* the generalized gradient approximation (GGA) in the scheme of Perdew-Burke-Ernzerhof [57]. Norm-conserving pseudopotentials [58] were employed for each atomic species with the following valence configurations: Li $2s^1$, Na $2s^2 2p^6 3s^1$, K $3s^2 3p^6 4s^1$, Ba $5s^2 5p^2 6s^2$, Ti $3p^6 3d^2 4s^2$, V $3p^6 3d^3 4s^2$, Nb $4p^6 4d^4 5s^1$, Ta $5p^6 5d^3 6s^2$, Mo $4p^6 4d^5 5s^1$, W $5d^4 6s^2$, O $2s^2 2p^4$ and F $2s^2 2p^5$, respectively. A plane-wave cut-off energy more than 940 eV was set throughout the calculations. To achieve a good convergence of electronic structures and optical properties, the dense K -points sampling of less than $0.025 \text{ \AA}^{-1}$ for the nine target compounds were adopted. The other calculated parameters used and convergent criteria were in line with the default values of the CASTEP code. Our tests reveal that the mentioned above computational parameters are sufficiently accurate for the present calculations.

At a zero frequency, the formula of second-order NLO coefficients can be described as [59–62]:

$$\chi^{\alpha\beta\gamma} = \chi^{\alpha\beta\gamma}(\text{VE}) + \chi^{\alpha\beta\gamma}(\text{VH}), \quad (1)$$

where,

$$\chi^{\alpha\beta\gamma}(\text{VH}) = \frac{e^3}{2\hbar^2 m^3} \sum_{vv'c} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[p_{vv'}^\alpha p_{v'c}^\beta p_{cv}^\gamma \right] \left(\frac{1}{\omega_{cv}^3 \omega_{v'c}^2} + \frac{2}{\omega_{vc}^4 \omega_{cv'}} \right), \quad (2)$$

$$\chi^{\alpha\beta\gamma}(\text{VE}) = \frac{e^3}{2\hbar^2 m^3} \sum_{vcc'} \int \frac{d^3k}{4\pi^3} P(\alpha\beta\gamma) \text{Im} \left[p_{vc}^\alpha p_{cc'}^\beta p_{c'v}^\gamma \right] \left(\frac{1}{\omega_{cv}^3 \omega_{v'c}^2} + \frac{2}{\omega_{vc}^4 \omega_{c'v}} \right), \quad (3)$$

here, α, β, γ are Cartesian components, v and v' denote valence bands, c and c' denote conduction bands, and $P(\alpha\beta\gamma)$ denotes full permutation. The band energy difference and momentum matrix elements are denoted as $\hbar\omega_{ij}$ and P_{ij}^α , respectively.

RESULTS AND DISCUSSION

Crystal structure and electronic structure

As mentioned above, there are 39 noncentrosymmetric d^0 TMOFs in the ICSD, and their crystal system distribution is shown in Fig. 1a. The 39 compounds crystallize in monoclinic (9 compounds, account for 23.0%), orthorhombic (19, 49.0%), trigonal (2, 5.0%), tetragonal (7,

Figure 1 Distribution of the 39 noncentrosymmetric d⁰ TMOFs (a) and proportion of all d⁰ TMOFs (b).

18.0%), hexagonal (1, 2.5%) and cubic (1, 2.5%) crystal systems, respectively. Accordingly, the orthorhombic crystal system is one of the most favorable systems. Generally, the band gap is enlarged due to the absence of d-d or f-f electron transitions in alkali/alkaline earth metals. Therefore, we focused on nine ATMOFs, with the proportion of 23.1% in the d⁰ TMOFs as shown in Fig. 1b, i.e., Na₃NbOF₆ [63], K₃Ti(O₂)₂F₃ [64], KNaNbOF₅ [48,65], NaVO₂F₂ [66], K₂TiOF₄ [67], Ba₂TiOF₆ [68], Ba₂MoO₃F₄ [69], Ba₂WO₃F₄ [69] and Li₂Ta₂O₃F₆ [70].

Since the nine compounds possess different fluorooxo-functional groups, according to the connection types of their fluorooxo-functional groups, they can be divided into three types as shown in Table 1. (i) All structures of type I have zero dimensional (0D) isolated fluorooxo-functional groups including NbOF₆, Ti(O₂)₂F₃ and NbOF₅ in Na₃NbOF₆, K₃Ti(O₂)₂F₃ and KNaNbOF₅, respectively. (ii) Type II includes NaVO₂F₂, K₂TiOF₄, Ba₂TiOF₆, Ba₂MoO₃F₄ and Ba₂WO₃F₄, with their fluorooxo-functional groups forming 1D infinite chains. (iii) Type III contains one compound Li₂Ta₂O₃F₆, in which the fluorooxo-functional TaO₃F₃ groups build up a six-member ring Ta₆O₁₂F₁₈ with vertex-sharing oxygen atom

to form 2D layers. Representatives of the three types of crystal structures are shown in Fig. 2a–c and all structures of the nine compounds are given in Fig. S1.

In general, a large band gap commonly corresponds to a high LDT for a crystal. Band gaps of the nine compounds are investigated by the gradient-corrected functional (GGA) and HSE06 hybrid functional. As shown in Fig. S2 and Table S2, results *via* HSE06 calculations can give more accurate prediction close to experimental band gaps. For the three compounds in type I, their computational band gaps adopted by HSE06 hybrid functional are 6.57, 4.23 and 5.65 eV for Na₃NbOF₆, K₃Ti(O₂)₂F₃ and KNaNbOF₅, respectively. For type II, the HSE06 band gaps of NaVO₂F₂, K₂TiOF₄, Ba₂TiOF₆, Ba₂MoO₃F₄ and Ba₂WO₃F₄ are 3.76, 3.21, 6.15, 3.45 and 4.13 eV, respectively. Li₂Ta₂O₃F₆ in type III has a HSE06 band gap of 5.49 eV. The GGA band structures of all compounds are shown in Fig. S3, and the GGA computational values are smaller than HSE06 gaps. The HSE06 gaps results demonstrate that the nine crystals can be considered as viable for application in IR region in terms of high LDT.

To clarify the electronic states which are related to optical properties, we plotted density/partial density of

Table 1 Classification of the nine ATMOFs (A = IA/IIA metals, TM = Ti, V, Nb, Ta, Mo and W)

Classification	Formula	Space group	fluorooxo-functional groups [TMOF]
Type I	Na ₃ NbOF ₆	<i>P2₁2₁2₁</i>	0D isolated NbOF ₆
	K ₃ Ti(O ₂) ₂ F ₃	<i>Cmc2₁</i>	0D isolated TiO ₄ F ₃
	KNaNbOF ₅	<i>Pna2₁</i>	0D isolated NbOF ₅
Type II	NaVO ₂ F ₂	<i>P2₁</i>	1D infinite chains
	K ₂ TiOF ₄	<i>Pna2₁</i>	1D infinite chains
	Ba ₂ TiOF ₆	<i>Cc</i>	1D infinite chains
	Ba ₂ MoO ₃ F ₄	<i>Cc</i>	1D infinite chains
	Ba ₂ WO ₃ F ₄	<i>Cc</i>	1D infinite chains
Type III	Li ₂ Ta ₂ O ₃ F ₆	<i>P3₁21</i>	2D layers

Figure 2 Crystal structures of 0D Na₃NbOF₆ (a), 1D NaVO₂F₂ (b), 2D Li₂Ta₂O₃F₆ (c), HSE06 band gaps (d), and the largest SHG coefficients (calculated) of the nine ATMOFs (A = IA/IIA metals, TM = Ti, V, Nb, Ta, Mo and W) (e).

states as well as the orbitals near the Fermi level as shown in Figs S4 and S5. The states of the nine ATMOF compounds indicate that the region of -5 eV to the Fermi level is mainly occupied by d^0 TM 3d/4d/5d, O 2p and F 2p orbitals. To better understand the bonding behavior of the nine compounds, bond order and Mulliken population analyses were performed. The bond order and Mulliken population analysis results indicate that the d^0 TM–(O and F) bonds have more covalent characteristic than the IA/IIA metals–(O and F) bonds (Table S3).

Optical properties of ATMOFs

As an outstanding IR NLO material, it should exhibit a high LDT (commonly large band gap, namely $E_g \geq 3.0$ eV) and large SHG responses ($d_{ij} \geq 10 \times \text{KDP}$) [21,29,31–34]. The HSE06 band gaps of the nine crystals are larger than 3.0 eV, and such results reveal that they

possess high LDT (Fig. 2d). Besides, their NLO coefficients were estimated by the first-principles calculations as shown in Table 2 and Fig. 2e. According to Fig. 2e, their NLO coefficients can be divided into three regions. The first region is smaller than $1 \times \text{KDP}$, as in K₃Ti(O₂)₂F₃, NaVO₂F₂ and Li₂Ta₂O₃F₆. The second region includes four compounds, Na₃NbOF₆, Ba₂TiOF₆, K₂TiOF₄ and KNaNbOF₅, whose NLO responses are comparable to $1 \times \text{KDP}$. The third region in Ba₂MoO₃F₄ and Ba₂WO₃F₄ possesses large NLO coefficients, more than $10 \times \text{KDP}$. In addition, the calculation results of Ba₂MoO₃F₄ and Ba₂WO₃F₄ are also consistent with the experimental ones [69], indicating the accuracy of our computations.

The computational birefringences Δn of the nine ATMOFs are relatively large (most $\Delta n > 0.07$, listed in Table 2). The birefringence is related to the anisotropy of the constituent elements [71–73]. Usually, contributions

Table 2 Calculated NLO coefficients and birefringence Δn of the nine ATMOFs (A = IA/IIA metals, TM = Ti, V, Nb, Ta, Mo and W)

Formula	NLO coefficients (pm/V)	Δn (@1064 nm)
Na ₃ NbOF ₆	$d_{14} = d_{25} = d_{36} = -0.40$	0.1440
K ₃ Ti(O ₂) ₂ F ₃	$d_{15} = d_{31} = 0.004$, $d_{24} = d_{32} = 0.002$, $d_{33} = -0.001$	0.1972
KNaNbOF ₅	$d_{15} = d_{31} = -0.44$, $d_{24} = d_{32} = 0.30$, $d_{33} = 0.72$	0.0447
NaVO ₂ F ₂	$d_{14} = 0.05$, $d_{16} = -0.02$, $d_{22} = 0.05$, $d_{23} = 0.04$	0.4684
K ₂ TiOF ₄	$d_{15} = d_{31} = 0.10$, $d_{24} = d_{32} = 0.62$, $d_{33} = -0.07$	0.1468
Ba ₂ TiOF ₆	$d_{11} = -0.16$, $d_{12} = -0.24$, $d_{13} = 0.29$, $d_{15} = 0.48$, $d_{24} = 0.13$	0.1360
Ba ₂ MoO ₃ F ₄	$d_{11} = 3.37$, $d_{12} = -2.17$, $d_{13} = -3.47$, $d_{15} = 2.1$, $d_{24} = 3.3$, $d_{33} = -5.7$	0.1052
Ba ₂ WO ₃ F ₄	$d_{11} = 2.96$, $d_{12} = -2.01$, $d_{13} = -2.32$, $d_{15} = 1.26$, $d_{24} = 2.33$, $d_{33} = -5.7$	0.0856
Li ₂ Ta ₂ O ₃ F ₆	$d_{11} = -d_{12} = -d_{26} = 0.15$	0.0948

to the birefringence Δn from the IA/IIA-metal cations can be ignored. To explore the origin of large birefringences, the anisotropy values $\Delta\alpha$ of the fluorooxo-functional groups [TMOF] were computed (Table S4). According to Table S4, the values $\Delta\alpha$ of the fluorooxo-functional groups [TMOF] are comparable to those of the famous units BO_3 , GaS_4 , PO_3F and PO_2F_2 , etc., indicating that the fluorooxo-functional groups [TMOF] possess strong polarizability anisotropy.

Functionality of fluorooxo-functional groups

Up to now, to the best of our knowledge, there are three fluorooxo-functional groups as NLO active units including [BOF], [POF] and [SiOF] for exploring excellent DUV NLO materials [27,41–42]. As discussed above, the nine ATMOFs demonstrate wide band gaps and large optical properties attributing to the fluorooxo-functional groups [TMOF], and here we mainly discuss ten fluorooxo-functional groups [TMOF] based on the investigation ICSD (Tables S4 and S5). The energy gaps and first order hyperpolarizabilities of four kinds of fluorooxo-functional groups ([TMOF], [BOF], [POF], [SiOF]) were calculated by Gaussian 09 package [74] under the condition of the B3LYP at LanL2DZ ([TMOF]) or 6-31G basis set ([BOF], [POF], [SiOF]), as shown in Fig. 3 and Table S4. According to Fig. 3, the fluorooxo-functional groups [BOF], [POF] and SiF_6 cover the energy range larger than 6.2 eV, which achieves the DUV region. Meanwhile, the ten fluorooxo-functional groups [TMOF] as IR NLO units expand the energy range from 3.5 to 6.2 eV. As a result, the energy band gaps of eight fluorooxo-functional groups, including VO_2F_2 , MoO_3F_3 , WO_3F_4 , TiO_4F_3 , MoO_3F_4 , $\text{Ta}_2\text{O}_3\text{F}_6$, TiOF_4 and NbOF_5 , span from 3.5 to 4.5 eV. In addition, the remaining two fluorooxo-functional groups TiOF_6 and NbOF_5 are in the region from 4.5 to 6.2 eV. Calculated results indicate that the energy gaps of the ten fluorooxo-functional groups [TMOF] are comparable to those of the typical mid-IR diamond-like units MS_4 ($\text{M} = \text{Al}, \text{Ga}, \text{Si}, \text{Ge}, \text{P}$). As is known, d^0 TM, oxygen and fluorine often form polyhedra, especially octahedra [50–53]. In the ten fluorooxo-functional groups [TMOF], molybdenum, oxygen and fluorine atoms can form the octahedra $\text{MoO}_x\text{F}_{6-x}$ ($x = 0, 1, 2, 3, 4, 5, 6$) [75]. It can be seen that the energy gaps of the fluorooxo-functional groups $\text{MoO}_x\text{F}_{6-x}$ ($x = 0, 1, 2, 3$) have very large highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gaps around 3.5 eV, while the $\text{MoO}_x\text{F}_{6-x}$ ($x = 4, 5, 6$) units have narrow energy gaps (< 1.5 eV).

The first order hyperpolarizabilities of the ten fluoro-

Figure 3 Calculated energy gaps and the largest first order hyperpolarizabilities of fluorooxo-functional groups including [TMOF], $\text{MoO}_x\text{F}_{6-x}$ ($x = 0, 1, 2, 3, 4, 5, 6$), [BOF], [POF] and SiF_6 , diamond-like groups MS_4 ($\text{M} = \text{Al}, \text{Ga}, \text{Si}, \text{Ge}, \text{P}$).

oxo-functional groups [TMOF] are large (Fig. 3). According to the values, the ten fluorooxo-functional groups [TMOF] can be divided in two parts. The first part contains five fluorooxo-functional groups $\text{Ta}_2\text{O}_3\text{F}_6$, TiO_4F_3 , NbOF_5 , NbOF_6 and MoO_3F_3 , and their first order hyperpolarizabilities are 47.9, 109.1, 202.5, 215.1 and 286.1 a.u., respectively. The second part includes five fluorooxo-functional groups, VO_2F_2 , WO_3F_4 , MoO_3F_4 , TiOF_4 and TiOF_6 , and their first order hyperpolarizabilities are 944.8, 975.5, 1298.5, 2522.4 and 2624.9 a.u., respectively. Compared with typical mid-IR diamond-like units MS_4 ($\text{M} = \text{Al}, \text{Ga}, \text{Si}, \text{Ge}, \text{P}$), the groups [TMOF] have comparable energy gaps and first order hyperpolarizabilities. For the NLO fluorooxo-functional groups [BOF] and [POF], the large first order hyperpolarizability also exhibits the superiority over BO_4 and PO_4 . According to Fig. 3, it shows an apparent hierarchy in band gaps and first order hyperpolarizabilities for the four kinds of fluorooxo-functional groups. As a result, [BOF] and [POF] can be as the DUV NLO active units, and the fluorooxo-functional groups [TMOF], demonstrating their potential superiority in designing mid-IR materials.

Therefore, the origin of SHG coefficients of the nine ATMOFs can be explained in terms of microscopic characteristic of fluorooxo-functional groups [TMOF]. As shown in Table S4, the fluorooxo-functional groups NbOF_6 , $\text{Ti}(\text{O})_2\text{F}_3$, NbOF_5 , VO_2F_2 , TiOF_4 , TiOF_6 and $\text{Ta}_2\text{O}_3\text{F}_6$ demonstrate large first order hyperpolarizabilities. However, the corresponding seven compounds

Na_3NbOF_6 , $\text{K}_3\text{Ti}(\text{O}_2)_2\text{F}_3$, KNaNbOF_5 , NaVO_2F_2 , K_2TiOF_4 , Ba_2TiOF_6 and $\text{Li}_2\text{Ta}_2\text{O}_3\text{F}_6$ exhibit small SHG responses which are smaller than or comparable to $1 \times \text{KDP}$. By analyzing their structures, it is found that the arrangements of corresponding NLO active FBBs are opposite (Fig. S1a–S1f, S1i). While in $\text{Ba}_2\text{MoO}_3\text{F}_4$ and $\text{Ba}_2\text{WO}_3\text{F}_4$, the fluorooxo-functional groups MoO_3F_4 and WO_3F_4 arrange along the same direction as shown in Fig. S1g and S1h, which gives rise to strong SHG response about $10 \times \text{KDP}$.

In order to verify whether ATMOFs reach mid-IR region, we calculated the vibrational frequencies of the fluorooxo-functional groups [TMOF] and the outstanding mid-IR FBBs (e.g., BS_3 , BS_4 , MS_4 ($M = \text{Al, Ga, Si, Ge, P}$)). Fig. 4 provides the largest vibrational frequencies and IR absorption edges of the fluorooxo-functional groups [TMOF], BS_3 , BS_4 , MS_4 ($M = \text{Al, Ga, Si, Ge, P}$). As a result, the IR absorption edges of the seven fluorooxo-functional groups [TMOF] including MoO_3F_3 , TiO_4F_3 , TiOF_4 , TiOF_6 , MoO_3F_4 , WO_3F_4 and $\text{Ta}_2\text{O}_3\text{F}_6$ approach $10 \mu\text{m}$ which covers two atmospheric windows (3–5 and 8–10 μm). However, the IR absorption edges of the fluorooxo-functional groups NbOF_6 , NbOF_5 and VO_2F_2 are wider than $8 \mu\text{m}$ but shorter than $10 \mu\text{m}$ (Table S5). Compared with the famous crystals IR spectra (BaB_2S_4 , AgGaS_2 , LiGaS_2 and BaGa_4S_7) (Table S5 and Fig. S6), the IR absorption edges of the most fluorooxo-functional groups [TMOF] exhibit comparable superiority in the IR atmospheric windows. Besides, oxide-based crystals could be excellent candidates as they can be grown in an open system [38]. All above results indicate that the d^0 TMOFs could be able to act as a promising mid-IR material for producing coherent light in the mid-IR region.

Hypothetical $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W; X} = \text{F, Cl, Br, I}$)
Since the MoO_3F_3 units are typical fluorooxo-functional octahedra, here we designed seven hypothetical structures $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W; X} = \text{F, Cl, Br, I}$). The phonon spectra of $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W; X} = \text{F, Cl, Br, I}$) are shown in Figs S7 and S8. Our phonon calculations verify that $\text{Na}_3\text{MoO}_3\text{Cl}_3$, $\text{Na}_3\text{WO}_3\text{F}_3$ and $\text{Na}_3\text{WO}_3\text{Cl}_3$ are dynamically stable owing to the absence of an imaginary phonon mode from the whole Brillouin zone (Fig. S7). However, the computational phonon spectra of $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W; X} = \text{Br, I}$) (Fig. S8a–S8d) show that there is imaginary phonon in the Brillouin zone, which means that they are kinetically unstable, such as $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$ (Fig. S8e).

Here we calculated band gaps and optical performances of $\text{Na}_3\text{MoO}_3\text{Cl}_3$, $\text{Na}_3\text{WO}_3\text{F}_3$ and $\text{Na}_3\text{WO}_3\text{Cl}_3$ since they

Figure 4 Maximum vibrational frequencies and IR absorption edges of the fluorooxo-functional groups [TMOF], BS_3 , BS_4 , MS_4 ($M = \text{Al, Ga, Si, Ge, P}$) units.

are dynamically stable, as shown in Table S6. HSE06 hybrid functional can accurately estimate band gaps [76]. And the band gap values decrease as the ionic radius of the halide elements increase from F to Cl. The band gaps of $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W; X} = \text{F, Cl}$) are still close to 3.0 eV or larger than 3.0 eV, which means that they are possible to have large LDT [36]. Since the distorted TMO_3X_3 ($\text{TM} = \text{Mo, W; X} = \text{F, Cl}$) octahedra show strong anisotropy, they possess large birefringence (all the birefringence $\Delta n > 0.1$). Their band gaps, birefringence Δn and density/partial density of states are given in Fig. S9. Among the seven structures, $\text{Na}_3\text{WO}_3\text{F}_3$ is kinetically stable and exhibits good performance, which further proves that the fluorooxo-functional groups [TMOF] are an excellent group for designing mid-IR NLO materials.

CONCLUSIONS

In summary, we systematically studied the structures, electronic structures and optical properties of the alkali/alkaline earth metals d^0 TMOFs, and the corresponding fluorooxo-functional groups. The fluorooxo-functional groups [TMOF] with different d^0 configuration cations exhibit the balance between wide HOMO-LUMO energy gaps and large first order hyperpolarizabilities. And the computational birefringences Δn of the alkali/alkaline earth metals d^0 TMOFs are relatively large (most $\Delta n > 0.07$) stemming from large anisotropy values $\Delta\alpha$ of the fluorooxo-functional groups [TMOF]. Besides, IR absorption edges of the seven fluorooxo-functional groups [TMOF] including MoO_3F_3 , TiO_4F_3 , TiOF_4 , TiOF_6 , MoO_3F_4 , WO_3F_4 and $\text{Ta}_2\text{O}_3\text{F}_6$ are close to those of the famous groups MS_4 ($M = \text{Al, Ga, Si, Ge, P}$), which indicates that the corresponding d^0 TMOFs have the ability to cover two atmospheric windows (3–5 and 8–10 μm).

The fluorooxo-functional groups [TMOF] can be used as the NLO active units for exploring mid-IR NLO materials. Furthermore, we also designed a hypothetical structure $\text{Na}_3\text{WO}_3\text{F}_3$. Its calculated result further demonstrates that the fluorooxo-functional groups [TMOF] are excellent units for exploring mid-IR NLO materials. Therefore, the d^0 TMOFs can be as a potential exploration system for mid-IR NLO crystals.

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Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information The supporting data are available in the online version of the paper. Crystallographic data of noncentrosymmetric d^0 transition metal oxyfluorides; band gaps of the nine ATMOFs ($A = \text{IA/IIA}$ metals, $\text{TM} = \text{Ti, V, Nb, Ta, Mo}$ and W) calculated by GGA and HSE06; Mulliken charge population of different atoms in the nine ATMOFs; computational performances of the fluorooxo-functional groups [TMOF], [BOF], [POF], SiF_6 and MS_4 ($M = \text{Al, Ga, Si, Ge, P}$); vibrational frequencies and IR absorption edges of the fluorooxo-functional groups [TMOF], BS_3 , BS_4 , MS_4 ($M = \text{Al, Ga, Si, Ge, P}$) units, AgGaS_2 , LiGaS_2 , BaGa_4S_7 and BaB_2S_4 ; crystal structures of the three type ATMOFs; partial density of states of d^0 transition metals, O and F element of the nine ATMOFs; band structures of the nine ATMOFs calculated by GGA functional; density/partial density of states of the nine ATMOFs; computational IR spectrum of metal chalcogenides BaB_2S_4 , AgGaS_2 , LiGaS_2 and BaGa_4S_7 ; phonon spectra of $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W}$; $\text{X} = \text{F, Cl, Br, I}$) and $\text{Sr}_2\text{Be}_2\text{B}_2\text{O}_7$; computational band gap, density/partial density of states and birefringence Δn of $\text{Na}_3\text{TMO}_3\text{X}_3$ ($\text{TM} = \text{Mo, W}$; $\text{X} = \text{F, Cl}$).

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基于氟化功能基团的 d^0 过渡金属氟氧化物中红外非线性光学材料设计研究

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摘要 红外非线性光学晶体在光电器件、资源勘探和长距离激光通讯等领域具有极其重要的应用, 因此探索性能优异的新型红外非线性光学晶体材料已成为该领域的一个重要方向. 当前, 该领域面临的主要挑战之一是如何实现宽带隙和大倍频效应之间的平衡. 本文中, 我们提出一种设计策略, 即引入 d^0 过渡金属的氟化功能基团作为活性基元, 设计中红外非线性光学晶体材料. 通过对含 d^0 过渡金属氟氧化物的系统研究, 我们探索了这类氟化功能基团对带隙和倍频响应的影响机制. 研究发现 d^0 过渡金属的氟化功能基团有利于产生较大的带隙. 基于第一性原理计算, 我们分析了碱金属/碱土金属 d^0 过渡金属氟氧化物的光学性能, 它们具有宽的带隙($> 3.0 \text{ eV}$)和大的双折射率(> 0.07), 其中2个分别含W和Mo的氟氧化物也呈现了较强的倍频效应. 此外, 我们对比分析了其他氟化功能基团, 发现在基本构筑基元中引入氟离子有利于光学性能的提升. 由此说明, 这种具有优异氟化功能基团的 d^0 过渡金属氟氧化物, 可以作为探索新型中红外非线性光学的潜在体系.