Rational Design and Synthesis of New Nonlinear Optical Materials

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We are here！
XTIPC, Urumqi

OUTLINE

1. Background

2. Main Research Results

3. Further Work Plans

OUTLINE

1. Background

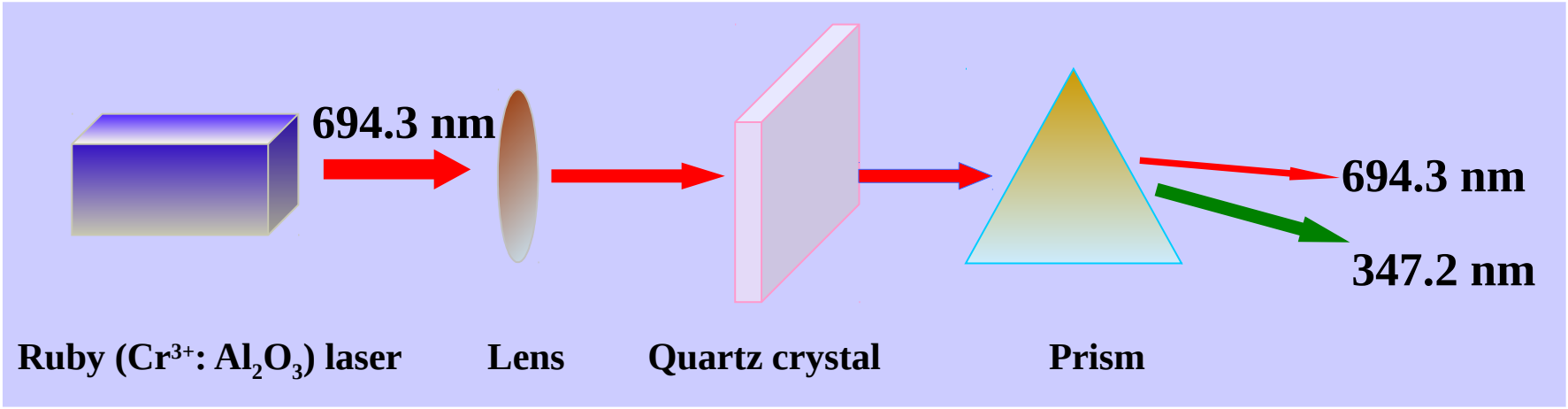
2. Main Research Results

3. Further Work Plans

1. Background

1.1 The development history of NLO crystal

- In 1960, Maiman[1] invented the ruby (Cr^{3+} : Al_2O_3) laser.
- The nonlinear optical (NLO) effect was first observed in 1961 by Franken[2]. Then the search for new NLO materials becomes the focus of research.



The experiment setup of frequency conversion

[1] T. H. Maiman, *Nature*, 1960, *187*, 493.

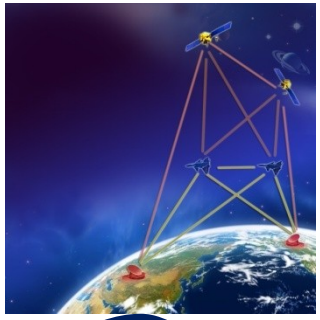
[2] P. A. Franken, et al, *Phys. Rev. Lett.*, 1961, *7*, 118.

1. Background

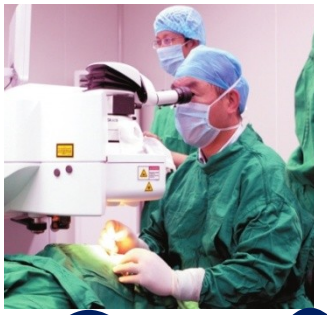
1.2 The applications of NLO crystal

- **NLO crystals are the key materials for the solid-state lasers to obtain UV/DUV coherent light.**

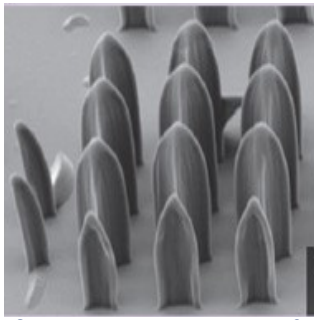
communication



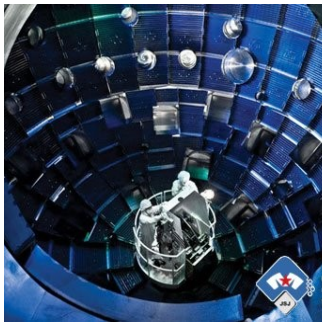
medicine



lithography



weapon



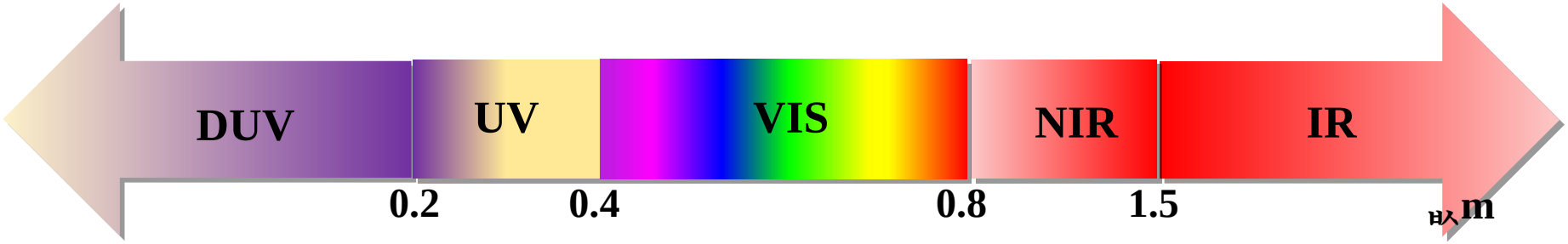
spark ignition

micromachining

1. Background

1.3 Development of inorganic NLO crystals

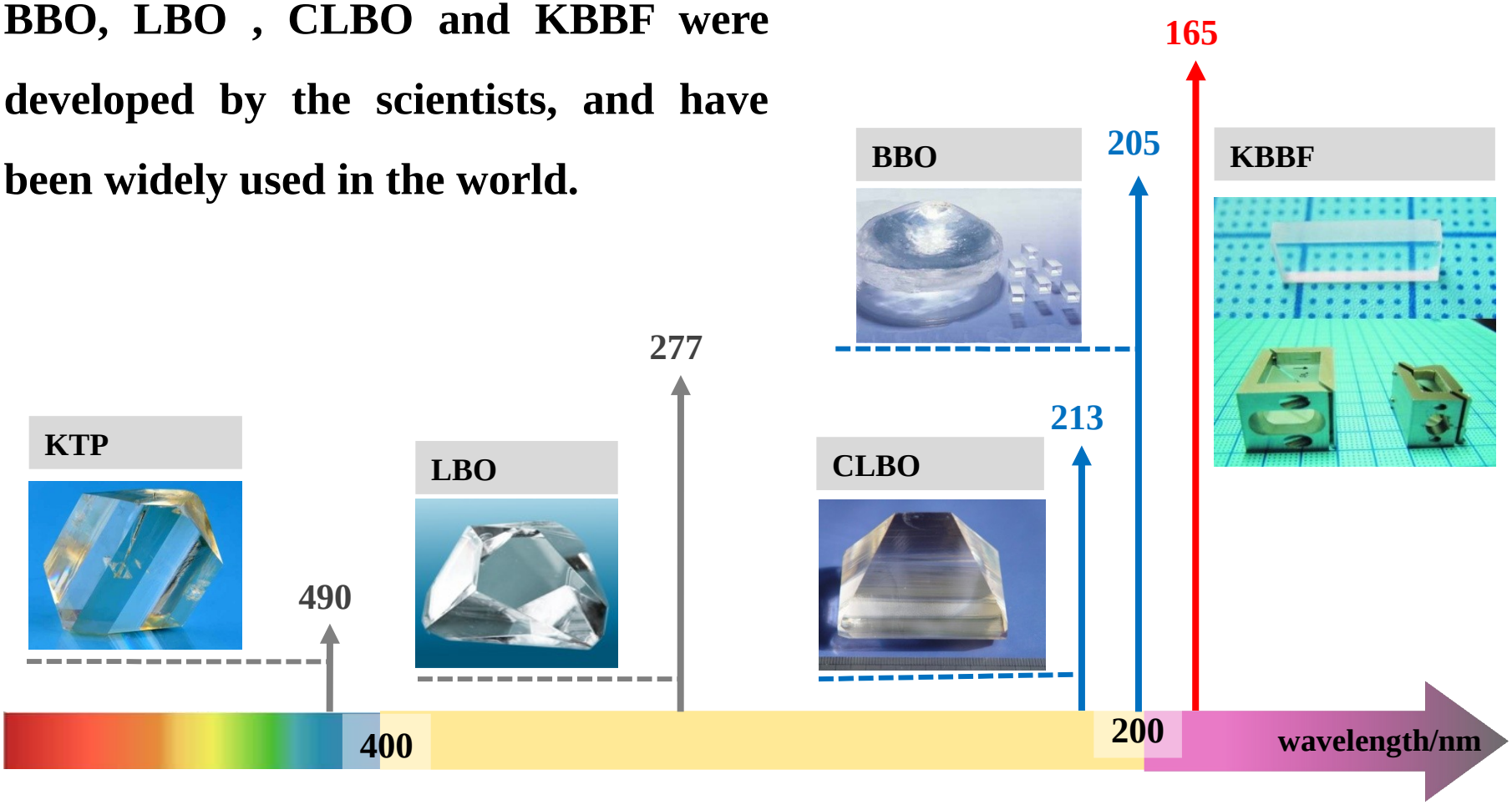
(D)UV	visible	infrared
CANNOT meet the demand	meet basic needs	laser-induced damage threshold (LIDT) need to be improved
Large SHG Response		
Short Cut-off Edge		
High laser-damaged threshold		
…		



1. Background

1.4 Commercial (D)UV NLO crystals

BBO, LBO , CLBO and KBBF were developed by the scientists, and have been widely used in the world.



1. Background

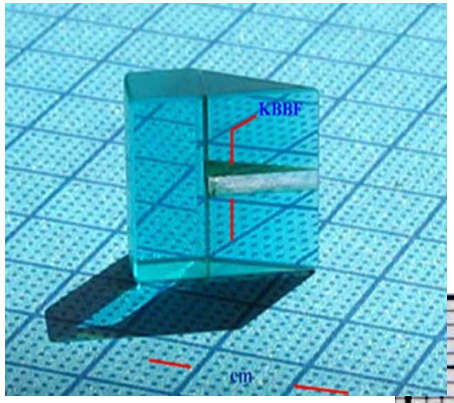
1.5 Commercial (D)UV NLO crystals

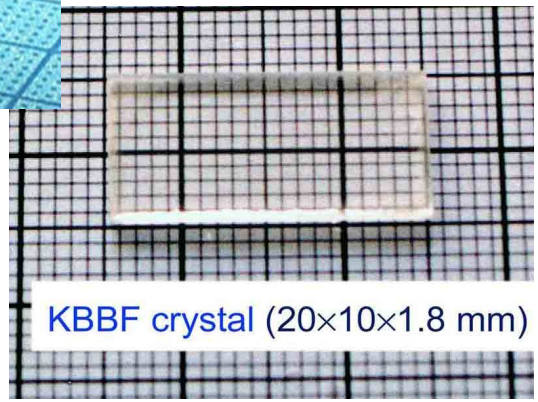
- **Till now, only KBBF allows straightforward sixth harmonic generation of 1064 nm (Nd:YAG) radiation: 177.3 nm (1064 nm/6)**

David Cyranoski report:

"CHINA'S CRYSTAL CACHE"

A Chinese laboratory is the only source of a valuable crystal.





However, KBBF contains highly toxic beryllium and shows a strong layering tendency, which limit the performance in DUV NLO applications.

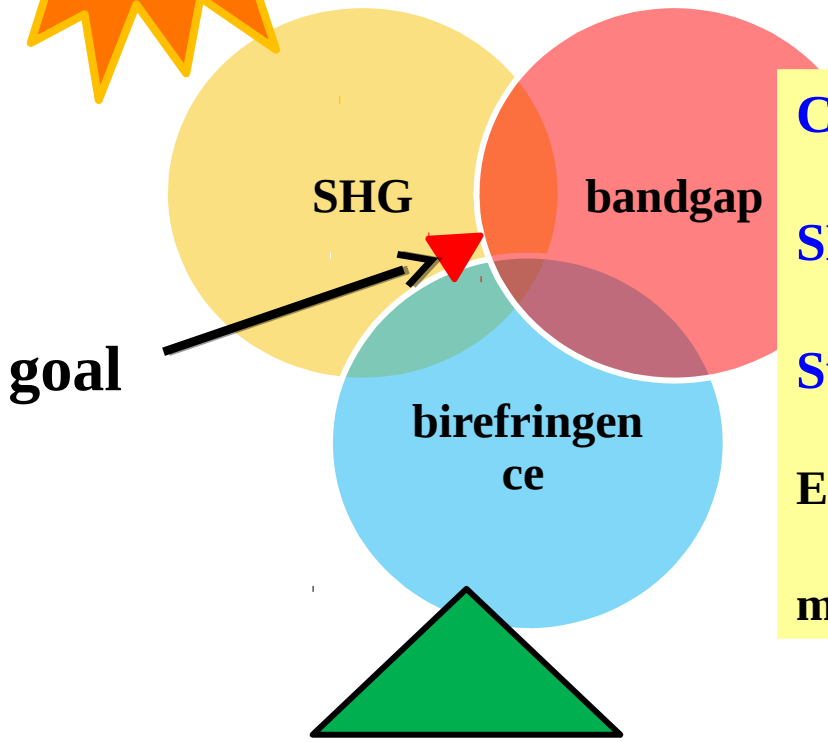
(Nature, 2009, 457, 953).

1. Background

1.6 Crucial requirements for DUV NLO materials

Challenge

Balance of "Bandgap-SHG-Birefringence"



Three Key factors

Cutoff edge < 200 nm

SHG response > 1KDP

Suitable birefringence for phase-matching

Easy to grow crystals and do not contain toxic raw material

1. Background

1.7 Research strategies

demands	strategies	examples	Pros	Cons
Large SHG	with Jahn-Teller cations	BiB_3O_6 $Pb_2B_5O_9I$	large distortion and SHG	red-shift the cutoff edge
Cutoff edge	introduce Be to remove BO_3 dangling bonds	KBBF family	shorter than 200 nm	toxic beryllium
birefringence	with π-conjugation BO_3, CO_3, and NO_3 units	KBBF $ABCO_3F$	Sufficient birefringence for phase-matching	strong layering tendency, difficult to grow

However, it is still a challenge to design an ideal DUV NLO crystal

OUTLINE

1. Background

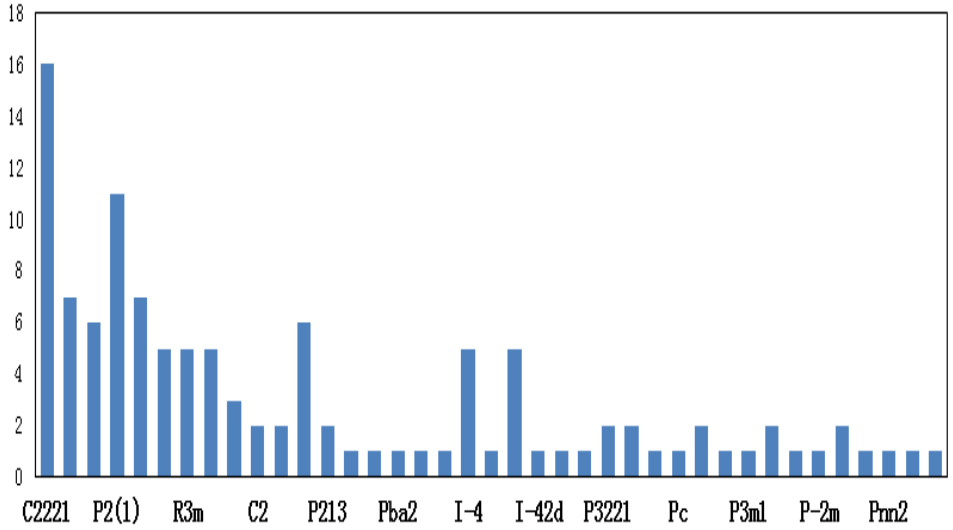
2. **Main Research Results**

3. Further Work Plans

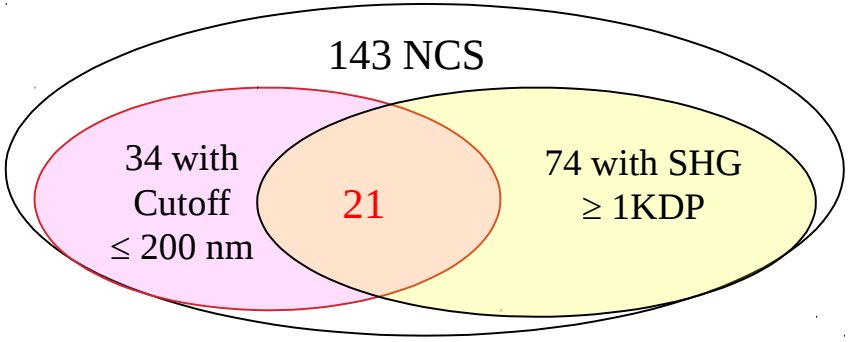
2. Main Research Results

2.1 Based on previous findings on NLO crystals

- **Set up a database containing advanced fundamental building units**

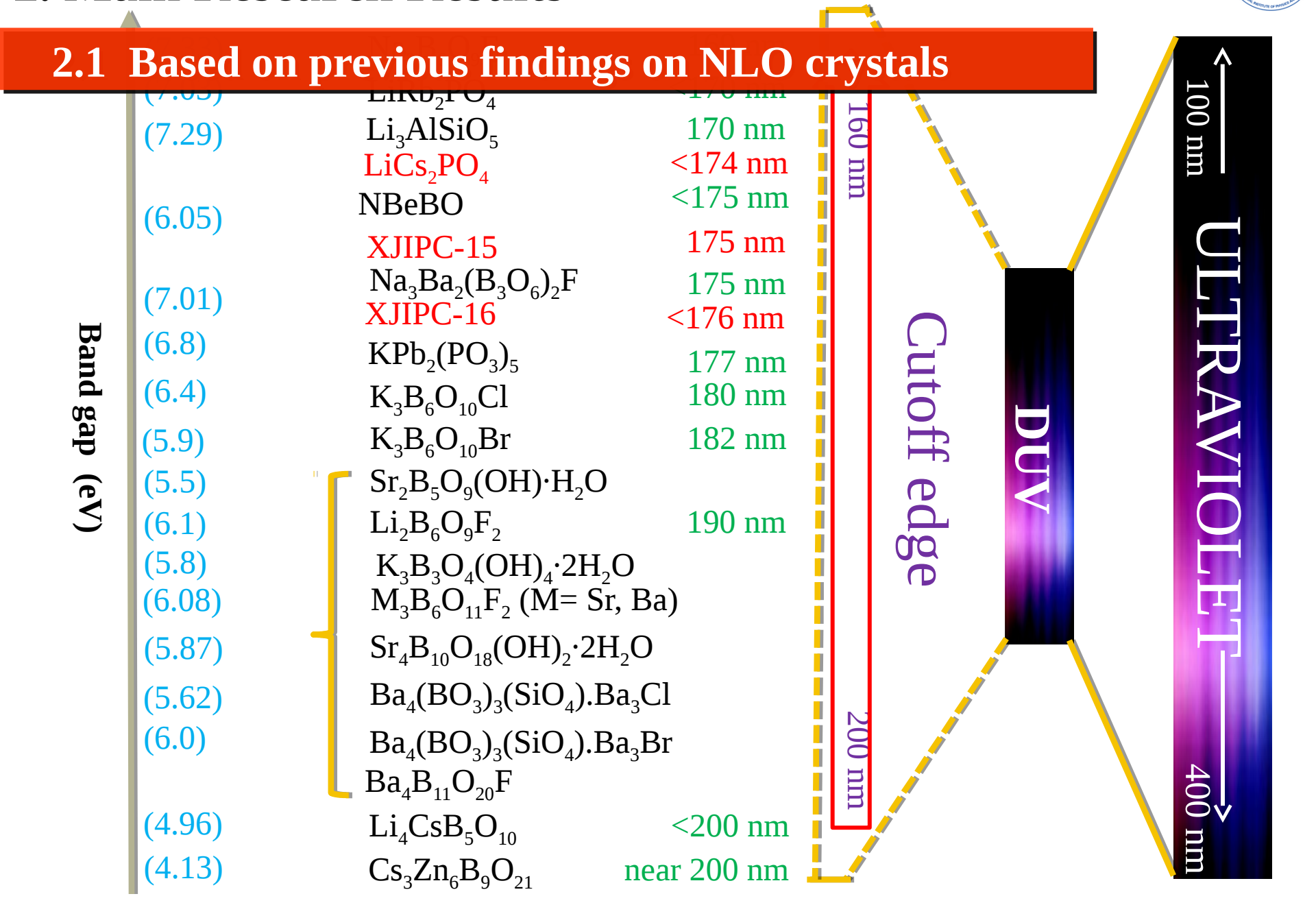


300+ new compounds



2. Main Research Results

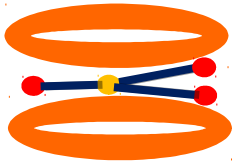
2.1 Based on previous findings on NLO crystals



2. Main Research Results

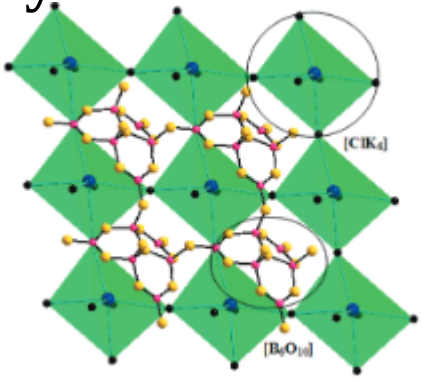
2.1 Based on previous findings on NLO crystals

Structure-property relationship analysis

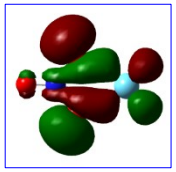


With π-conjugation

Large SHG



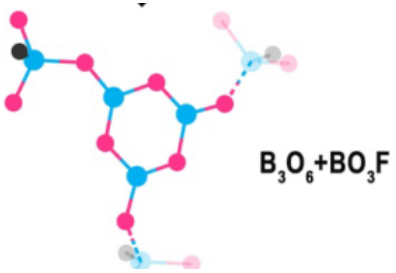
Perovskite-like structure

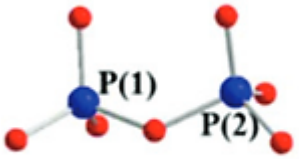


$Pb\text{-}BO_3$ connection

Short Cutoff edge

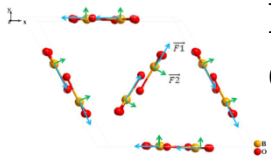
Remove dangling bonds



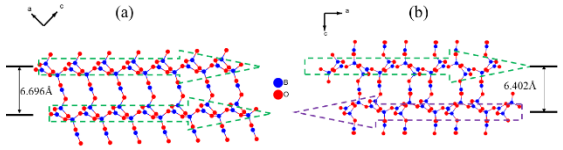


Tetrahedral units

Suitable birefringence

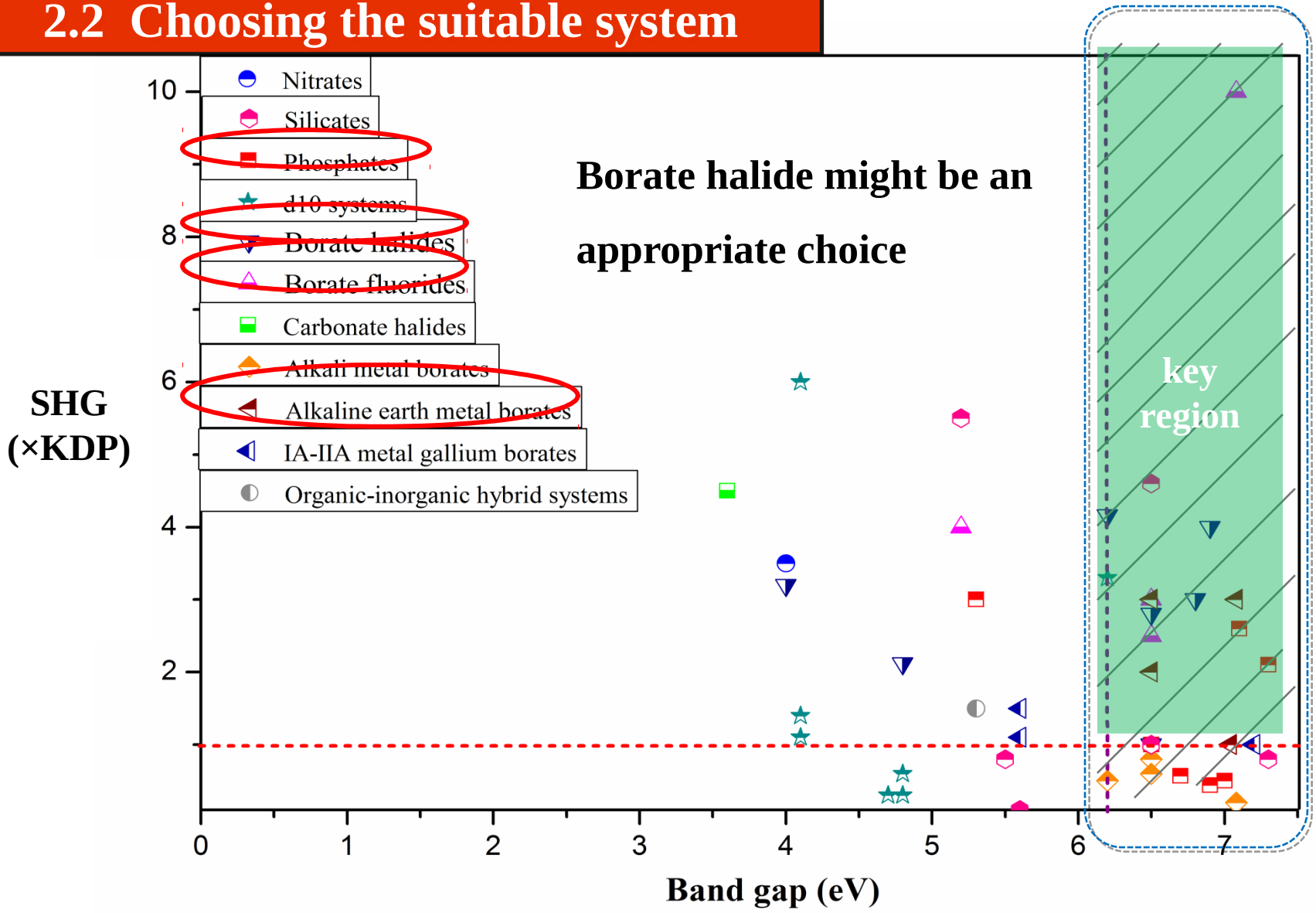


Preferred orientation



2. Main Research Results

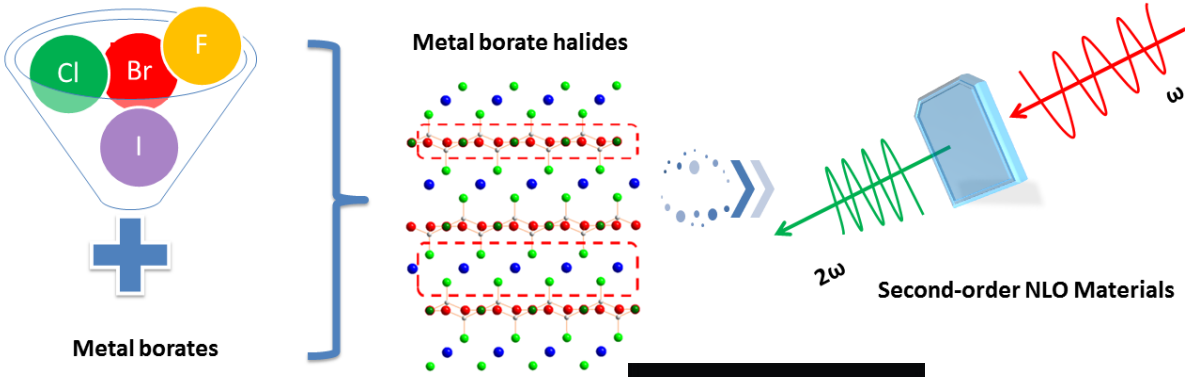
2.2 Choosing the suitable system

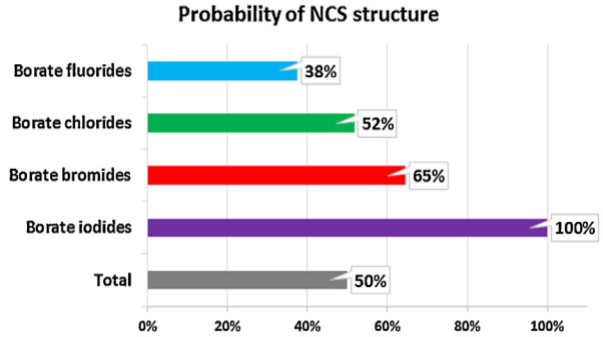


2. Main Research Results

2.2 Choosing the suitable system

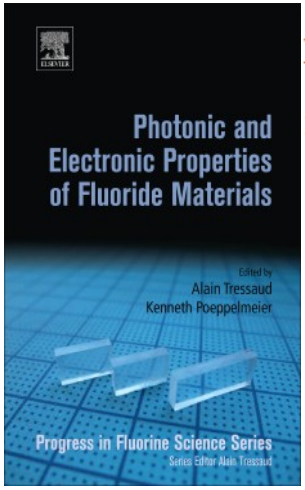
Recently discovered metal borate halides are summarized, including their synthesis, crystal structure features, properties and second-order NLO performances.





Elsevier Book chapter focusing on

F-containing metal borates



Part Four Non-linear Properties

15 Frequency-Doubling Oxide Fluorides, Borate Fluorides, and Fluorooxoborates

S. Pan, Y. Wang, K.R. Poeppelmeier

1. Introduction
2. Fundamentals of Borate Fluorides and Fluorooxoborates: Synthesis and Structural Chemistry
3. Borate Fluorides as Frequency-Doubling Materials
4. Fluorooxoborates as Frequency-Doubling Materials
5. Summary and Outlook

References

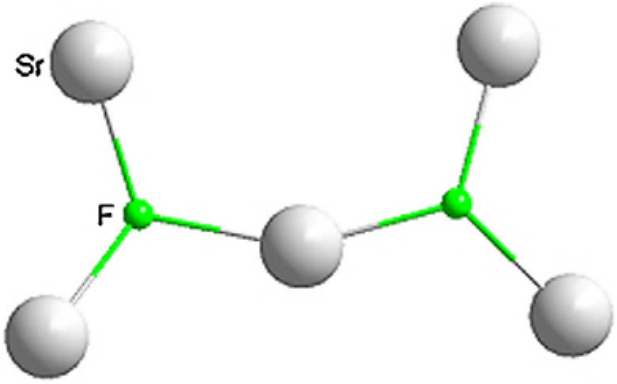
Coord. Chem. Rev. 2016, 323, 15; *Photonic and Electronic Properties of Fluoride Materials*, Elsevier, 2016

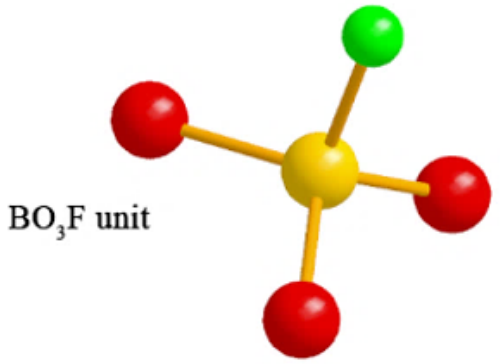
2. Main Research Results

2.3 New strategy for designing DUV NLO materials

F-containing metal borates can be divided into two types:

(1) Borate fluorides (or fluoride borates) are double salts, in which one (or more) fluorine atom is directly coordinated to the metal atoms, such as KBBF





(2) Fluorooxoborates (or simply fluoroborates) are anionic species, where one (or more) fluorine atom is directly coordinated to the B atoms, such as KBF_4, LiB_6O_9F, $Na_2B_6O_9F_2$, etc.

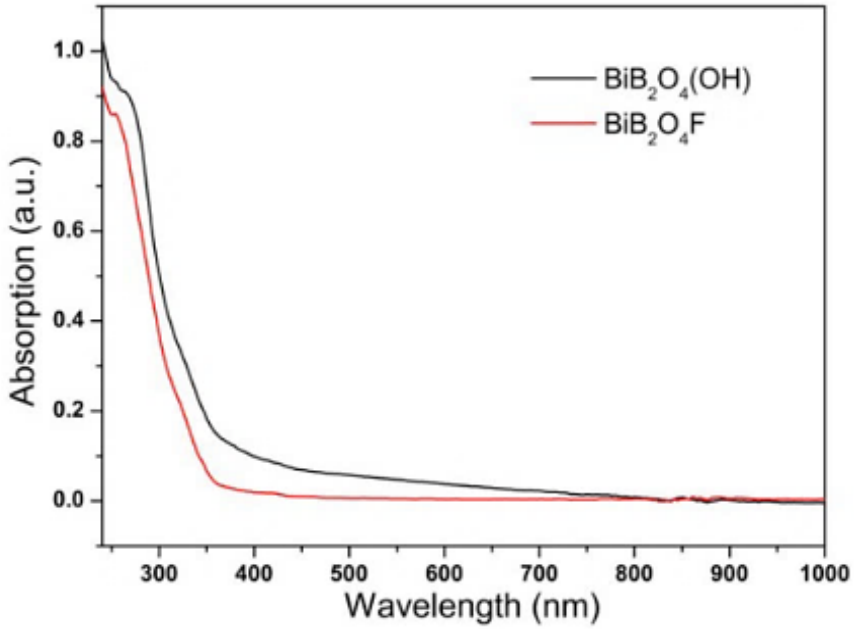
2. Main Research Results

2.3 New strategy for designing DUV NLO materials

Literature review： F atom is beneficial for large bandgap (short cutoff edge)

The large electronegativity of the fluorine atom requires higher energy for electronic excitation when irradiated under light

isostructural compounds (with O replaced by F atom) → cutoff edge blue shift



UV cutoff edge of BiBOF is 15 nm shorter than that of BiBOH

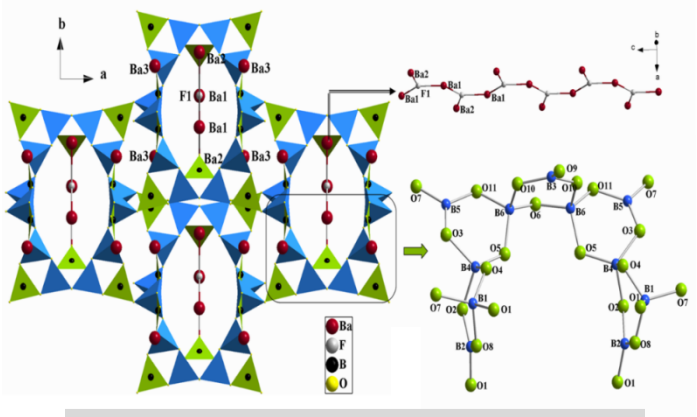
R. R. Cong. Z. S. Lin, C. T. Chen, et al. *Inorg. Chem. Front.*, 2015, *2*, 170.

2. Main Research Results

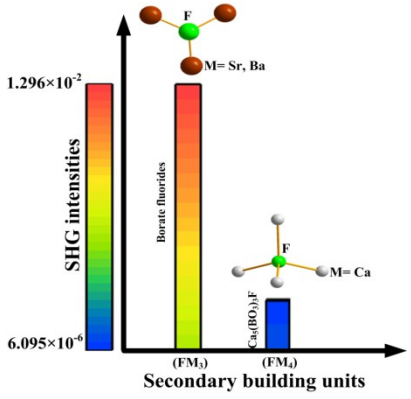
2.3 New strategy for designing DUV NLO materials

We have proven that F atom is beneficial for producing large SHG

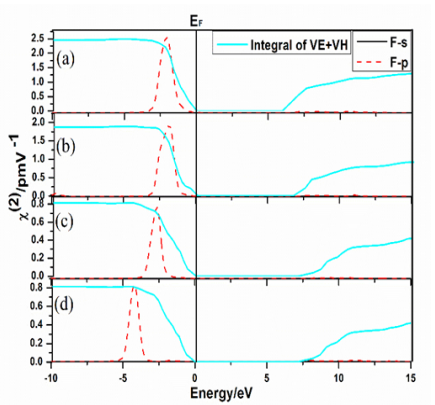
Because fluorine is the most electronegative atom, it is deduced that the electrons can be withdrawn toward F atoms leading to a higher local polarization.



BBOF with large SHG response



polar displacement



F atom contribution

Indirect contribution: polar displacement, producing large distortion

Direct contribution: quantify the F atom contribution to SHG by DFT

HongpingWu, Zhihua Yang, Shilie Pan*, et al, J. *Am. Chem. Soc.*, 2013, *135*, 4215
Ying Wang, Shilie Pan*, *Coord. Chem. Rev.* 2016, *323*, 15.
Beenish Bashir, Zhihua Yang*, Shilie Pan*, et al, *Cryst. Growth Des.*, 2016, *16*, 5067.

2. Main Research Results

2.3 New strategy for designing DUV NLO materials

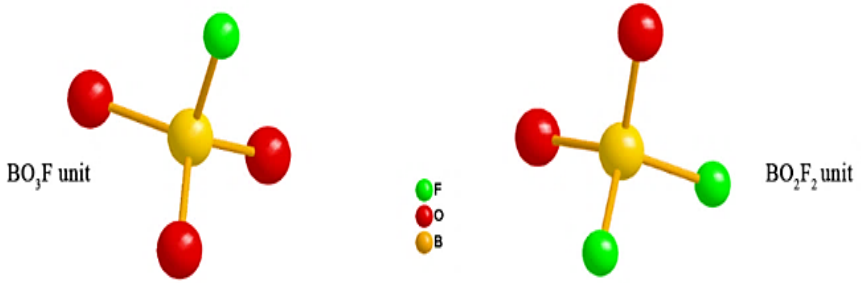
We also propose that F atom can increase the birefringence

Fluorooxoborates with B-F bonding contain new functional units: $BO_{4-x}F_x$ (x = 1 ~ 3)

Dipole moment (*P*), polarizability anisotropy (*δ*), hyperpolarizability (|*β*max|) and HUMO-LUMO gap (*E*g)

units	P_x, P_y, P_z	*δ*	$\lvert\beta_{max}\rvert$	E_g (eV)
$(BO_3F)^{4-}$	2.2, 0.0, 0.0	2.1	39.5	9.7
$(BO_2F_2)^{3-}$	0.0, 0.0, −2.3	3.4	82.6	9.2
$(BOF_3)^{2-}$	−1.8, 0.0, 0.0	2.5	30.9	9.5
$(BO_4)^{5-}$	0.0, 0.0, 0.0	0.0	4.1	10.7
$(BO_3)^{3-}$	0.0, 0.0, 0.0	7.1	10.8	8.5

DFT calculations reveal that $(BO_3F)^{4-}$, $(BO_2F_2)^{3-}$ and $(BOF_3)^{2-}$ units have a very large polarizability anisotropy and hyperpolarizability



Bingbing Zhang, Zhihua Yang*, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2017, *56*, 3916. (VIP)

2. Main Research Results

2.3 New strategy for designing DUV NLO materials

Fluorooxoborates

- Alkali/alkaline earth metal cation
  - ■ No *d-d* electron transitions in the UV region (high transmittance)
- B-O groups
  - ■ Large band gap, low two-photon absorption and high laser-induced damage threshold
  - ■ π -conjugated planar BO_3 is benefitial for large SHG response & moderate birefringence
- F atoms
  - ■ Blue-shift cutoff edge
  - ■ Generate large distortion & SHG
  - ■ Increase optical anisotropy and birefringence

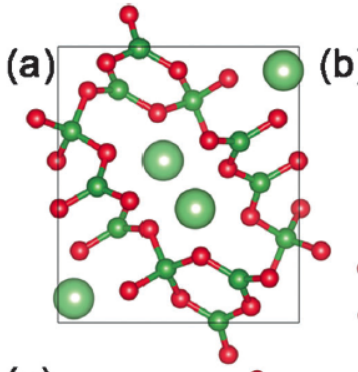
Fluorooxoborates: Beryllium-Free Deep-Ultraviolet Nonlinear Optical Materials

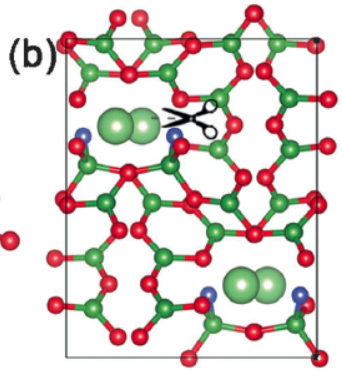
2. Main Research Results

2.4 Fluorooxoborates: $Li_2B_6O_9F_2$

- Using F atom to substitute O atom in LBO and obtaining a series of fluorooxoborates

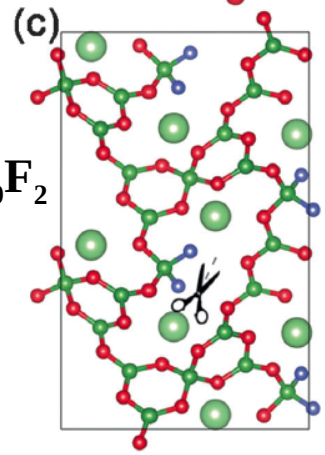
LBO

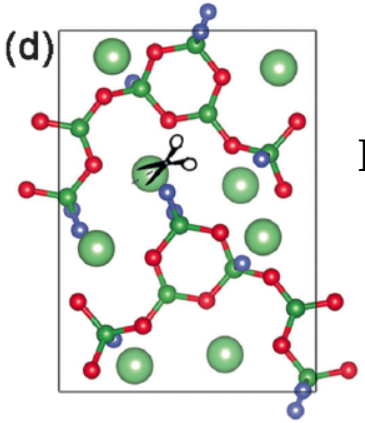




LiB_6O_9F

$Li_2B_6O_9F_2$





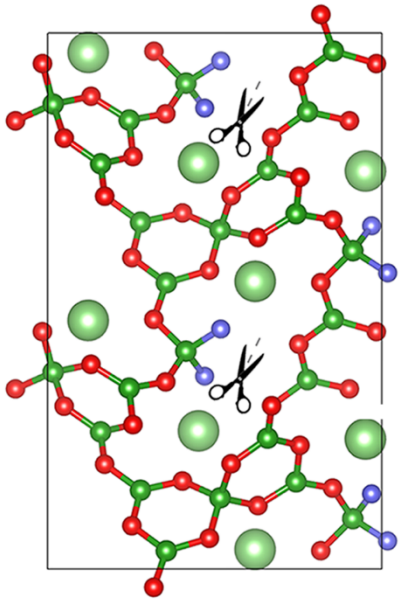
$Li_2B_3O_4F_3$

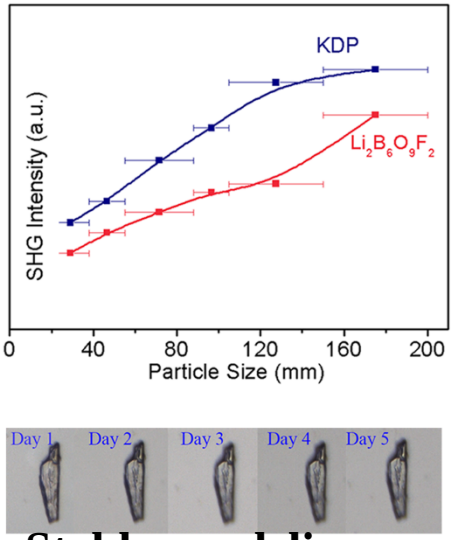
Introducing of the F atoms "cut through" the fixed 3D B–O network of LBO

2. Main Research Results

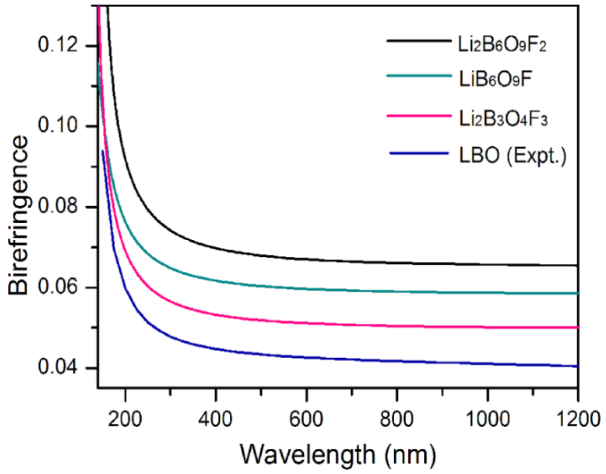
2.4 Fluorooxoborates: $Li_2B_6O_9F_2$

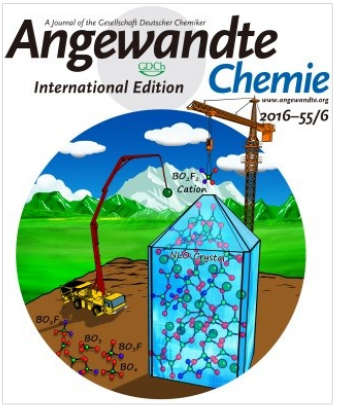
- The suitable candidate: $Li_2B_6O_9F_2$
- large birefringence~0.066 ， a predicted shortest type I SHG wavelength of 192 nm, shorter than that of LBO (277 nm).
- large SHG efficiency (0.9 × KDP), phase-matchable at 266 nm





Stable, no deliquescent





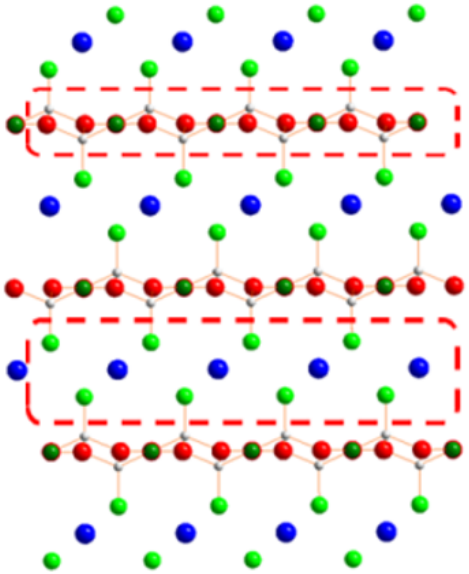
VIP

Bingbing Zhang, Zhihua Yang*, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2017, *56*, 3916. (VIP)

2. Main Research Results

2.5 Fluorooxoborates: AB_4O_6F family

From KBBF to AB_4O_6F (A = NH_4, Na, K, Rb, Cs) family



KBBF

Introduce new functional building units: BO_3F

Strategy： BeO_3F in KBBF is replaced by BO_3F

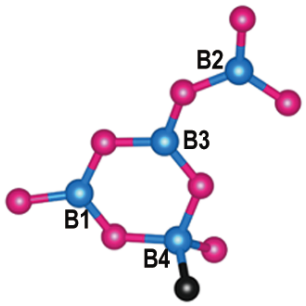
- **better growth habit owing to more compact structure**
- **higher NLO coefficients**
- **does not require toxic BeO**

AB_4O_6F inherits the excellent optical properties of KBBF and has significant advantages over KBBF

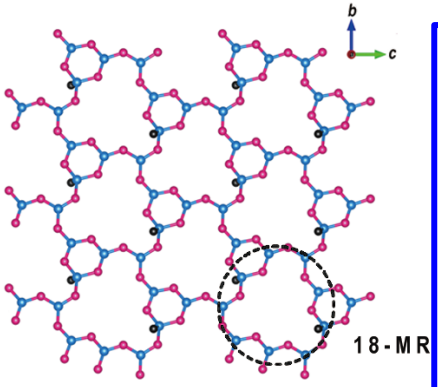
2. Main Research Results

2.5 Fluorooxoborates: ABF

Example 1: $NH_4B_4O_6F$ (ABF) （Space group *Pna*2_1, *a* = 7.602 Å, *b* = 11.197Å, *c* = 6.5952Å）



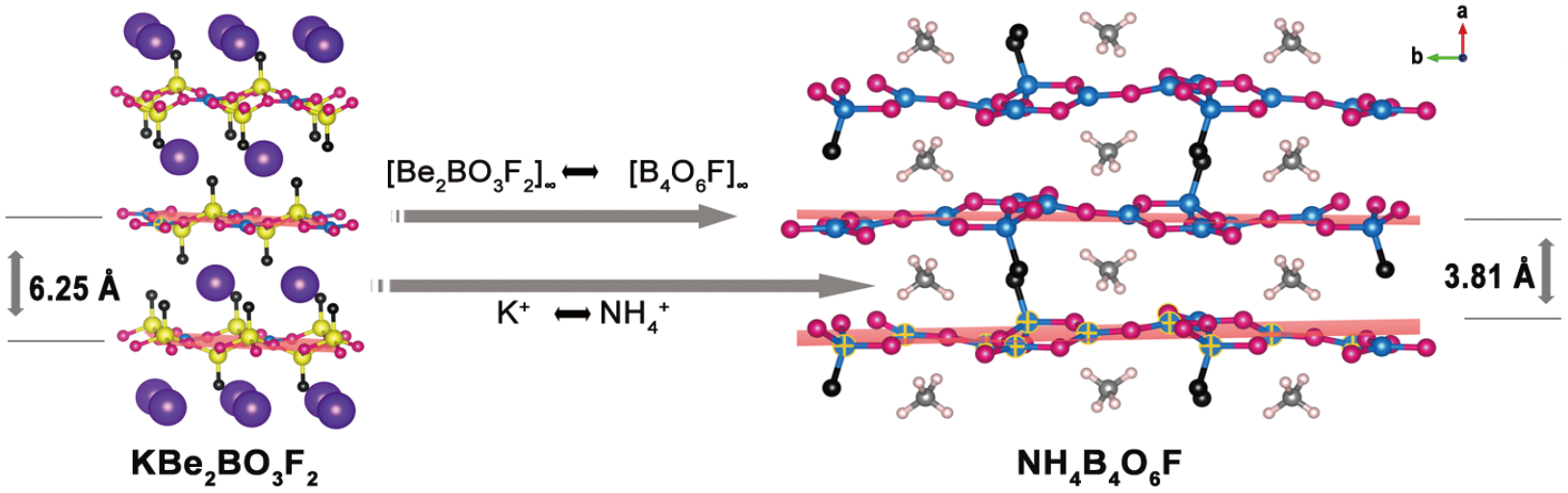
$[B_4O_8F]^{5-}$ building unit



$[B_4O_6F]_\infty$ layer

Superior to KBBF in two other aspects:

- ✓ **Half of interlayer spacing---improved growth habit**
- ✓ **Doubled BO_3 density---larger SHG response**

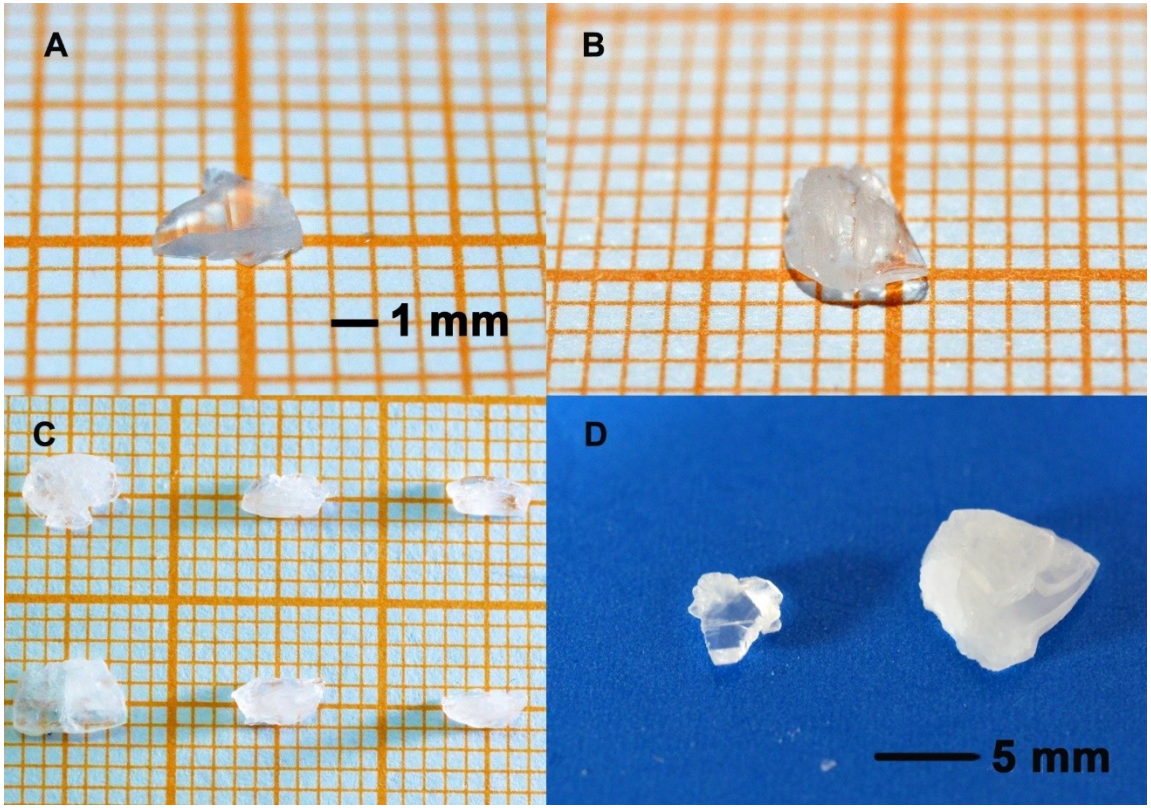


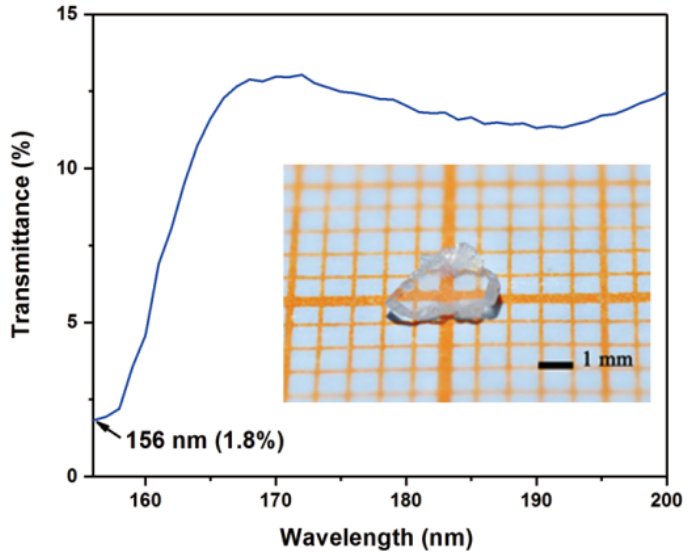
$KBe_2BO_3F_2$ $NH_4B_4O_6F$

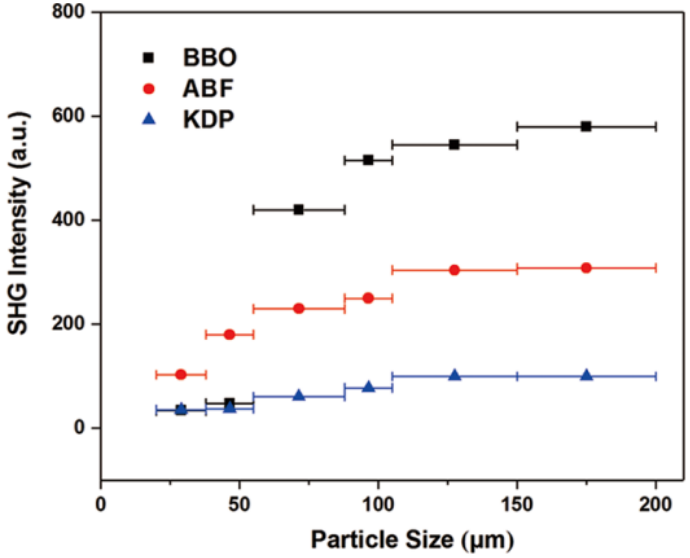
2. Main Research Results

2.5 Fluorooxoborates: ABF

- Easy to grow with little or no layer tendency
- Short cutoff edge (156 nm)
- Large SHG response (3×KDP & 0.5×BBO)







2. Main Research Results

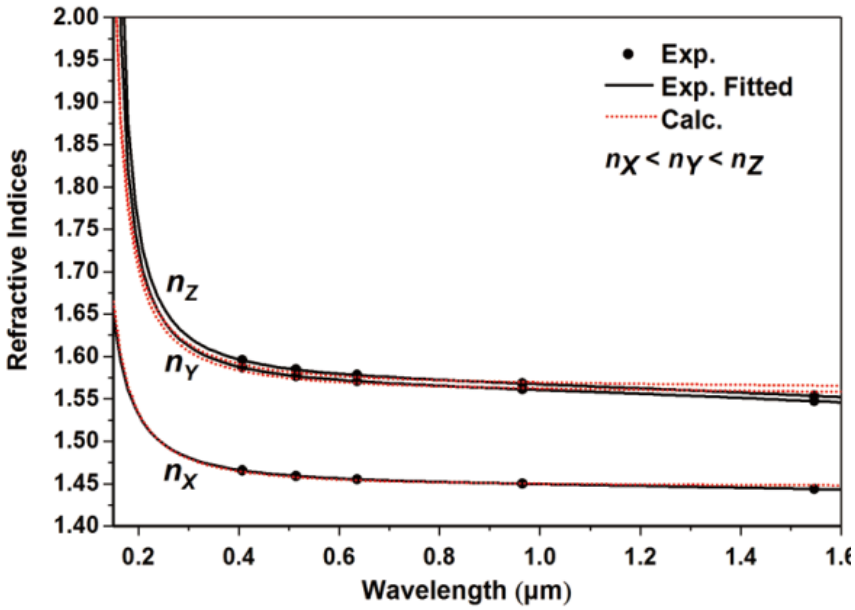
2.5 Fluorooxoborates: ABF

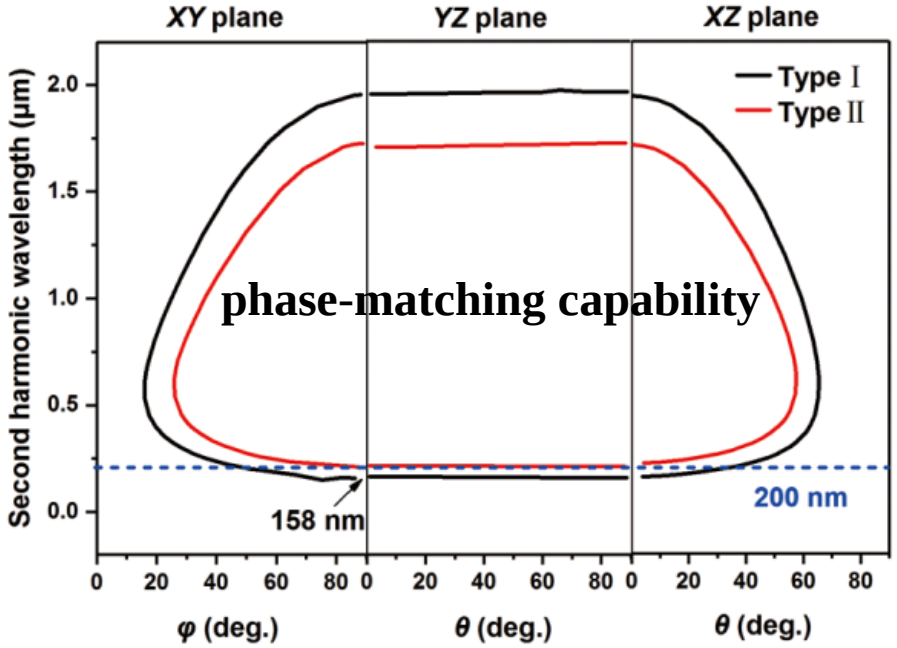
Sellmeier equations

$$n_x^2 = 2.10333 + \frac{0.00710}{\lambda^2 - 0.01094} - 0.00909 \times \lambda^2$$

$$n_y^2 = 2.45077 + \frac{0.01058}{\lambda^2 - 0.02000} - 0.02517 \times \lambda^2$$

$$n_z^2 = 2.47210 + \frac{0.01139}{\lambda^2 - 0.02130} - 0.02631 \times \lambda^2$$





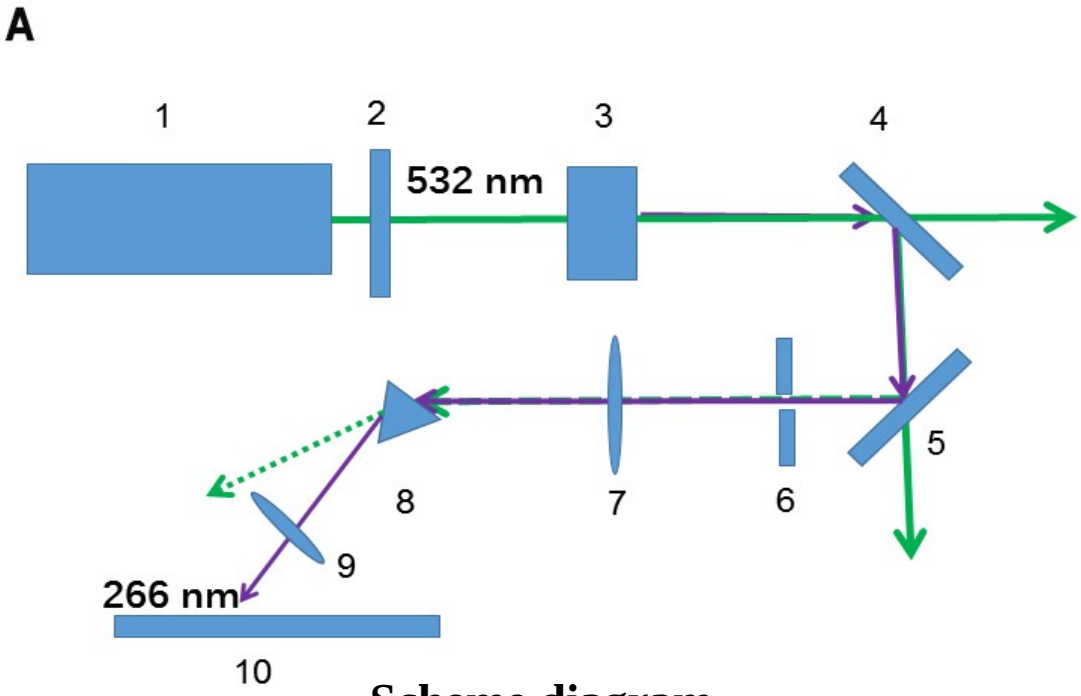
Shortest phase-matching SHG wavelength is 158 nm （*XY* plane）

Besides KBBF and RBBF, ABF is the another NLO crystal that can generate DUV coherent light below 200 nm by a direct SHG process

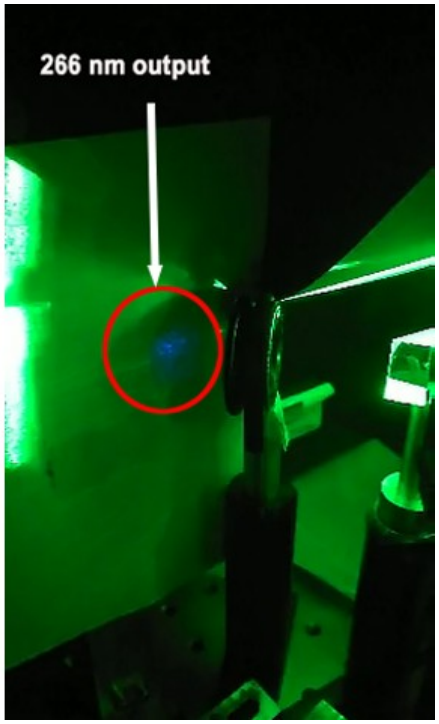
2. Main Research Results

2.5 Fluorooxoborates: ABF

Cooperate with Prof. Z.Y. Xu's research team (TIPC, CAS) and evaluate the fourth harmonic generation ability of ABF



Scheme diagram



266 nm output

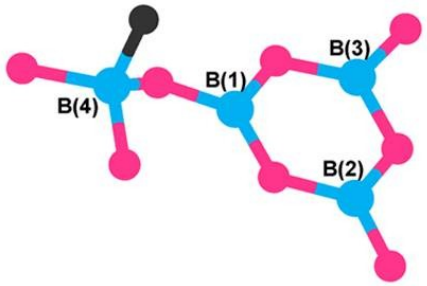
Further evaluation (e.g., shorter SHG wavelength) is under the way

Guoqiang Shi, Zhihua Yang, Shilie Pan*, et al, *J. Am. Chem. Soc.*, 2017, *31*, 10645.
Apply for Chinese and US Patents

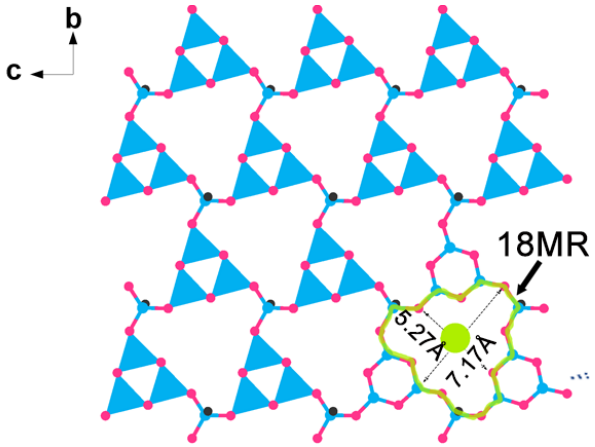
2. Main Research Results

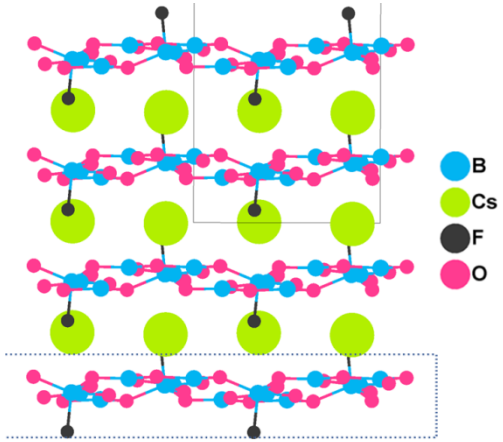
2.5 Fluorooxoborates: CBF

Example 2: CsB_4O_6F (CBF) (Space group *Pna*2_1, BUT shows a different structure)



$[B_4O_8F]$ group, which is composed of three BO_3 triangles forming B_3O_6 rings and one BO_3F tetrahedron

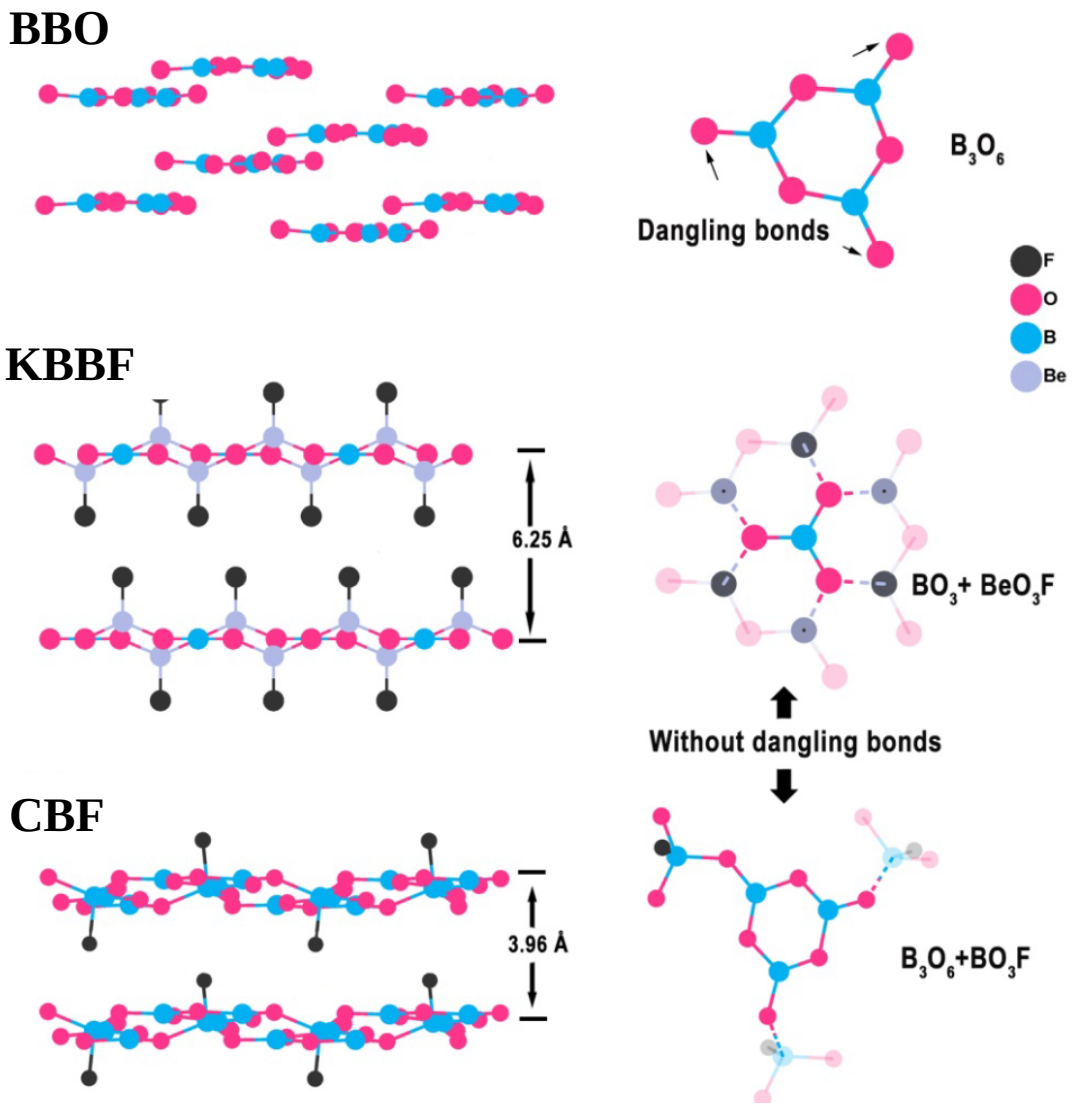




Like KBBF, it features a two-dimensional (2D) $[B_4O_6F]_\infty$ anionic layer with the Cs^+ cations residing between the layers

2. Main Research Results

2.5 Fluorooxoborates: CBF



CBF inherits the excellent *genes* of *β*-BBO and KBBF by introducing new $[B_4O_8F]$ functional units

Eliminate the *dangling bonds* of oxygens and enlarge the band gaps

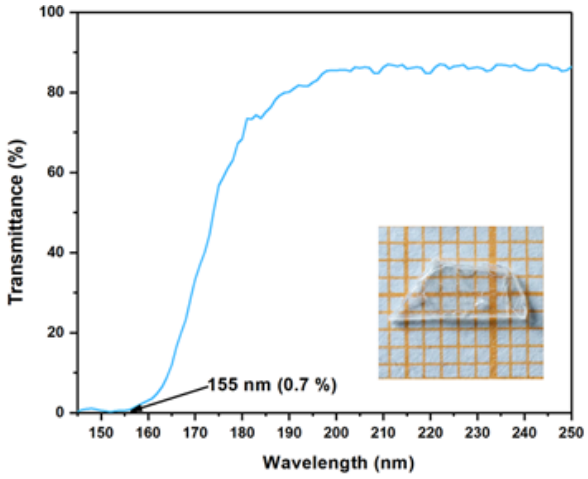
The distance of two adjacent layers largely reduces from 6.25 Å in KBBF to 3.96 Å in CBF.

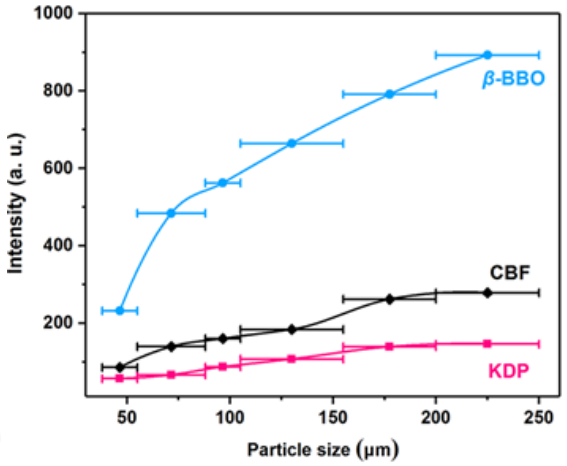
2. Main Research Results

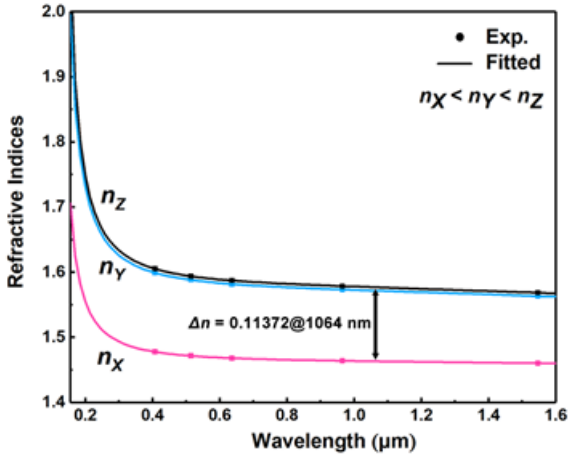
2.5 Fluorooxoborates: CBF

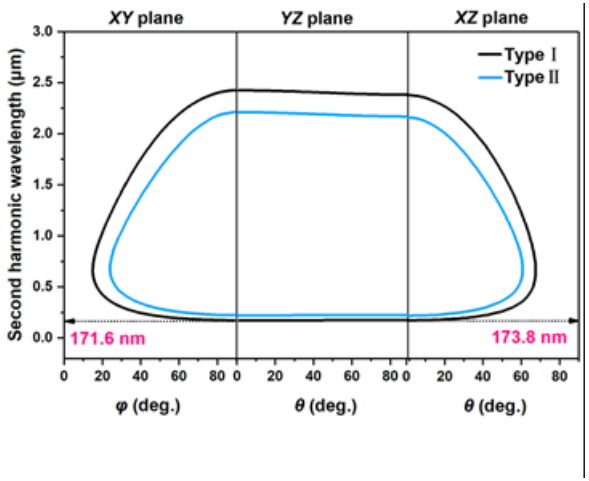
CBF also exhibits outstanding NLO properties

- **Short DUV cutoff edge (155 nm)**
- **Large NLO response (1.9 × KDP).**
- **Suitable birefringence (shortest PM second-harmonic wavelength ~171.6 nm)**



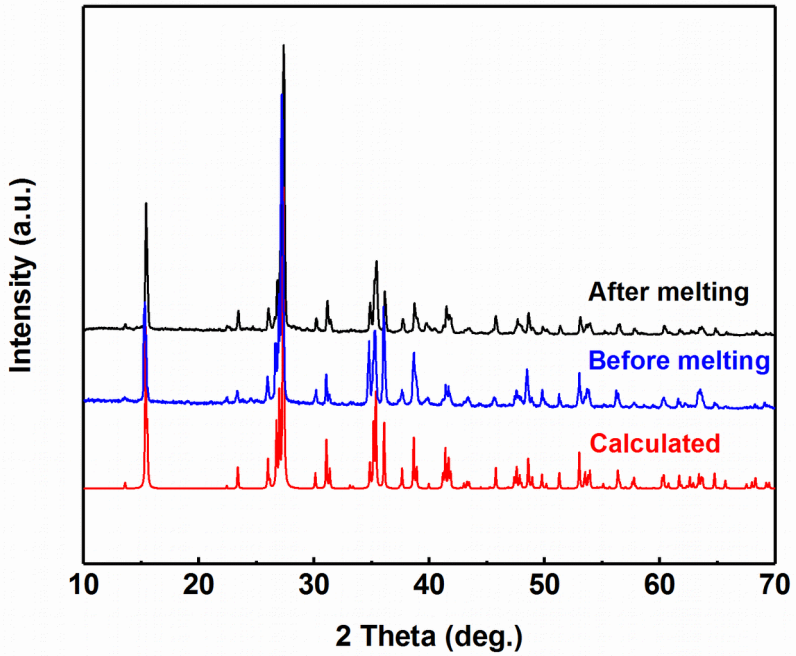






2. Main Research Results

2.5 Fluorooxoborates: CBF



CBF melts congruently, which is beneficial to crystal growth and industrial applications

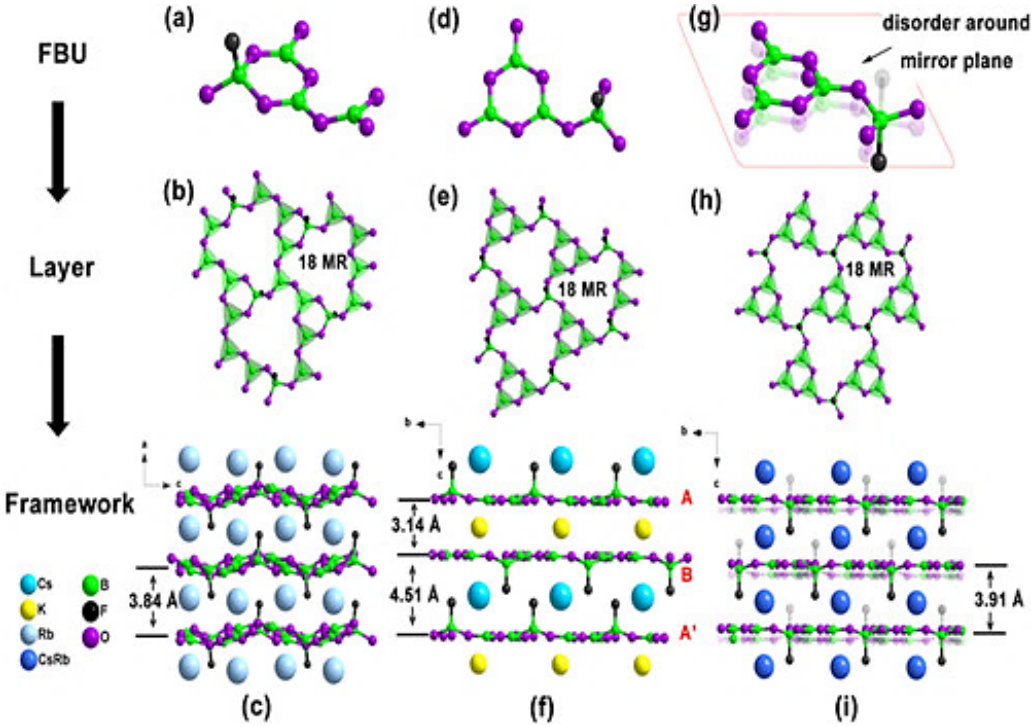
Xuefei Wang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2017, *56*, 14119.

Apply for Chinese and US Patents

2. Main Research Results

2.5 Fluorooxoborates: RBF/CKBF/CRBF

- Three new alkali metal fluorooxoborates were successfully synthesized



RbB_4O_6F (RBF) $CsKB_8O_{12}F_2$ (CKBF) $CsRbB_8O_{12}F_2$ (CRBF)

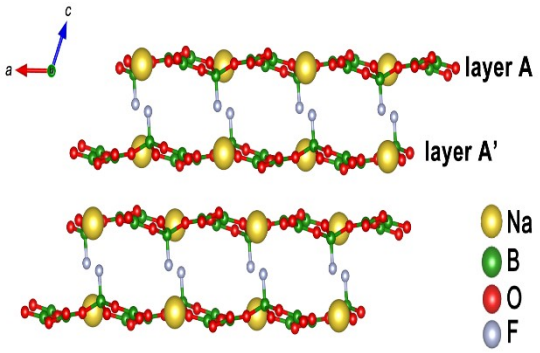
- By judicious selection of the A-site alkali metal cation, they show similar but different structures (space group: *Pna*2_1, *P*321 and *P*-*62c*)
- They exhibit excellent linear and NLO properties including short UV absorption edges (<190 nm), and large SHG responses ranging from 0.8 to 1.9 × KDP

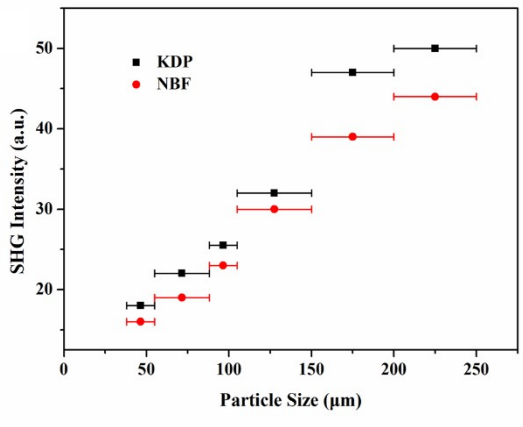
Ying Wang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2018, *57*, 2172.

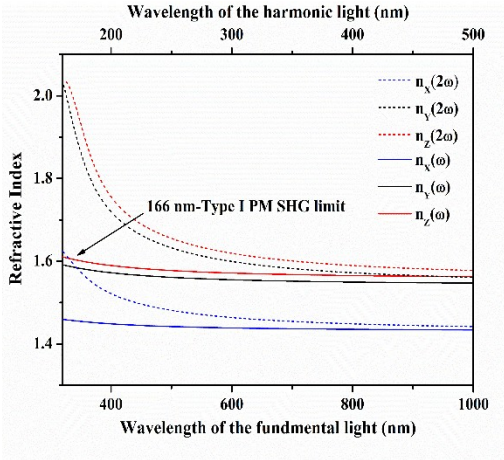
2. Main Research Results

2.5 Fluorooxoborates: NBF

Sodium Fluorooxoborate crystallizes in space group C2 and NaB_4O_6F exhibits outstanding NLO properties







Suitable SHG response (0.9 × KDP)

Shortest type I phase-matching wavelength (~166 nm)

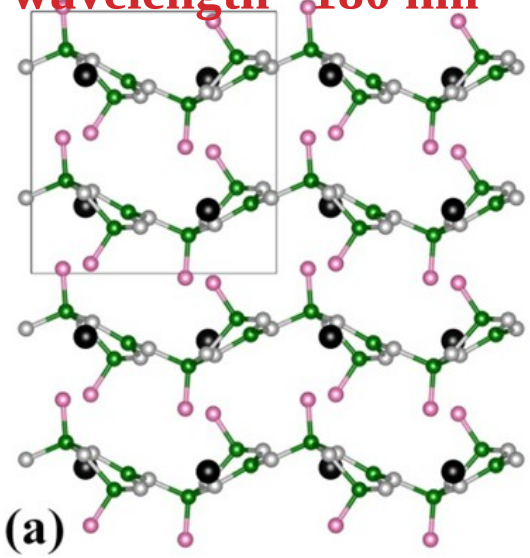
Zhizhong Zhang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.* 2018, *57*, 6577.

2. Main Research Results

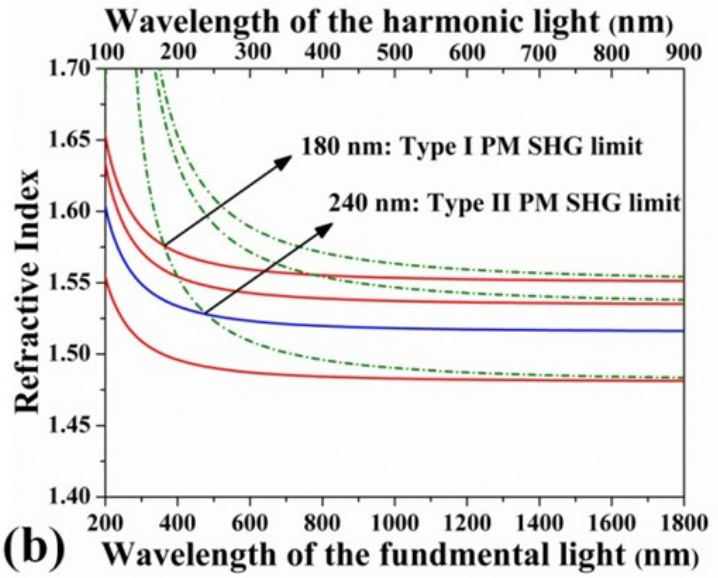
2.5 Fluorooxoborates: SBOF

The first case of NLO-active alkaline earth fluorooxoborates: $SrB_5O_7F_3$

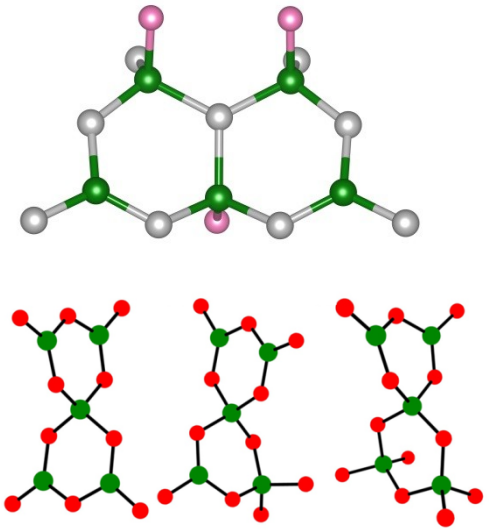
- $SrB_5O_7F_3$ crystallizes in space group $Cmc2_1$ and its UV cutoff edge <180 nm, SHG effect ~1.6×KDP, large birefringence (0.07@532), shortest phase-matching second harmonic wavelength ~180 nm



$SrB_5O_7F_3$ structure



phase-matching condition



$B_5O_9F_3$ double ring

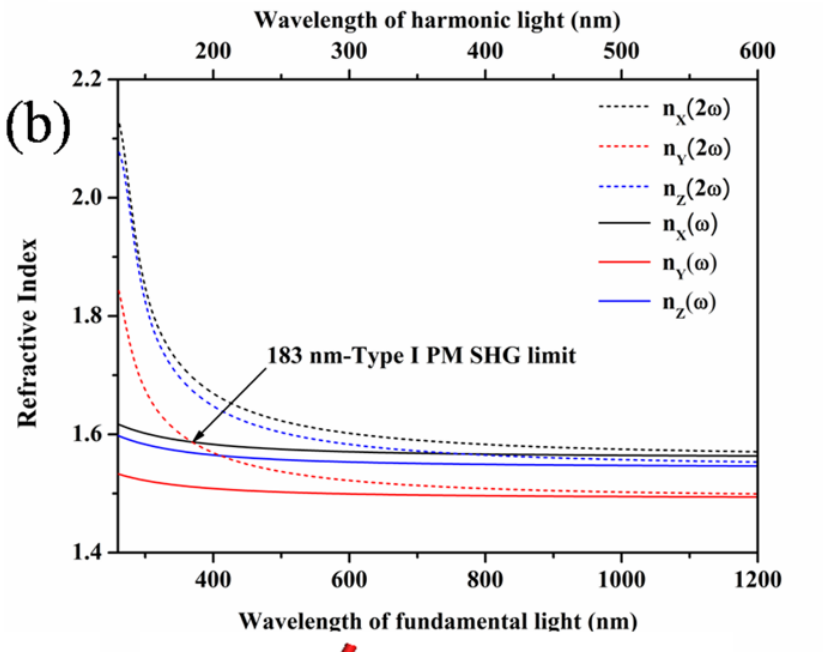
Miriding Mutailipu, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.* 2018, *57*, 6095. (Cover, VIP)

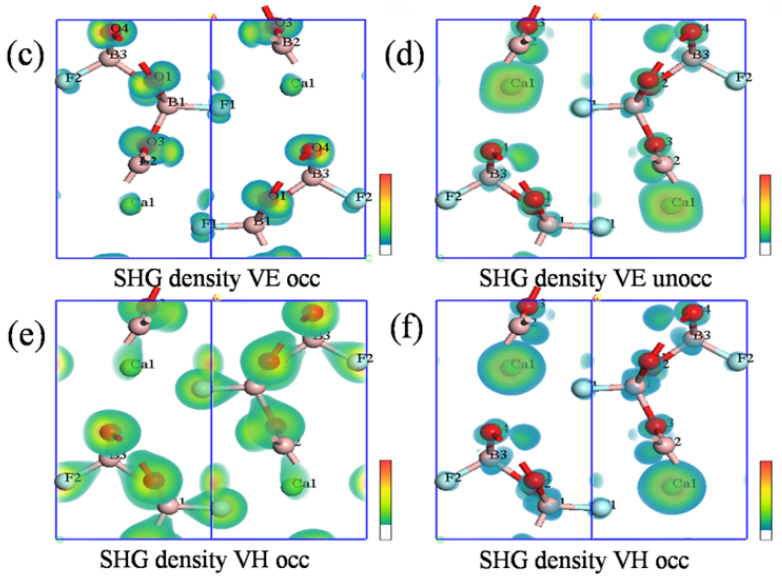
2. Main Research Results

2.5 Fluorooxoborates: CBOF

The Ca isomorph shows similar NLO performance

- $CaB_5O_7F_3$ UV cutoff edge <180 nm , SHG effect ~2×KDP (larger!) , shortest phase-matching second harmonic wavelength ~183 nm
- The enhanced SHG response originates from the contributions of $B_5O_9F_3$ double rings and Ca^{2+} cations





$CaB_5O_7F_3$ SHG density map

2. Main Research Results

2.5 Fluorooxoborates: summary

- **Fluorooxoborate crystals are promising DUV NLO materials**

*Calculated

Compounds	Absorption edge (nm) or band gap （eV）	SHG intensity (× KDP) (@1064 nm)	Shortest PM SHG wavelength (nm)	Feature
KBBF	147 (8.43）	1.2	162	Toxic raw material, layered structure
LiB_6O_9F	(8.37)*	~	-	
$Li_2B_6O_9F_2$	(8.05)*	0.9	192*	non-toxic, without layered tendency
$Li_2B_3O_4F_3$	(8.42)*	~	-	
$NH_4B_4O_6F$	156 (7.95)	3.0	158	
NaB_4O_6F	<180 (166)*	0.9	166*	
RbB_4O_6F	<200 (7.73)*	0.8	165*	
CsB_4O_6F	155 (8.00)	1.9	172	
$CsKB_8O_{12}F_2$	<200 (7.76)*	1.9	170*	
$CsRbB_8O_{12}F_2$	<200	1.1	~	
$CaB_5O_7F_3$	<180 (8.75)*	2.0	183*	
$SrB_5O_7F_3$	<180 (8.58)*	1.6	180*	

Bingbing Zhang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2017, *56*, 3916.
Guoqiang Shi, Zhihua Yang, Shilie Pan*, et al, *J. Am. Chem. Soc.*, 2017, *31*, 10645.
Xuefei Wang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2017, *56*, 14119.
Ying Wang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*, 2018, *57*, 2172.
Zhizhong Zhang, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.* 2018, *57*, 6577.

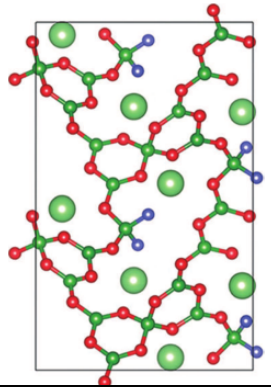
Two comments on “Chemical & Engineering News” (ACS):

Science Concentrates

MATERIALS

▶ Nonlinear optical laser material avoids beryllium

Materials scientists have developed a new class of deep-ultraviolet nonlinear optical (DUV NLO) crystals that promise to be less toxic and have better performance than the



$Li_2B_6O_9F_2$ offers deep-ultraviolet nonlinear optical properties without beryllium and debilitating layering.

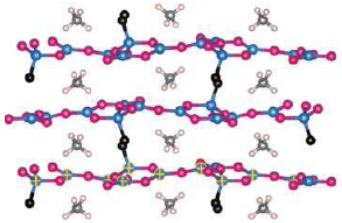
materials currently used (*Angew. Chem. Int. Ed.* 2017, DOI: 10.1002/anie.201700540). DUV NLO materials

c&en GLOBAL ENTERPRISE

MATERIALS

New borate crystal boosts UV optical applications

The ability of inorganic crystals known as nonlinear optical (NLO) materials to alter the properties of a beam of laser light—for example, doubling its frequency—makes them indispensable for applications in fiber optics, photolithography, and laser micromachining. Few NLO materials can generate coherent light deep in the ultraviolet range (< 200 nm). $KBe_2BO_3F_2$ (KBBF) is an exception. But the toxicity of beryllium and the low intensity of KBBF's NLO properties limit its application. A team of researchers led by Shilie Pan of Xinjiang Technical Institute of Physics & Chemistry and Kenneth R. Poeppelmeier of Northwestern University may have come up with a solution—$NH_4B_4O_6F$ (ABF), a beryllium-free deep-ultraviolet NLO material (*J. Am. Chem. Soc.* 2017, DOI: 10.1021/jacs.7b05943). The researchers report that ABF's nonlinear coefficients are roughly 2.5 times as large as KBBF's values. They also note that their synthesis method, based on the high-temperature reaction of B_2O_3 with NH_4F, leads to high-quality crystals that tend to be thicker than typical KBBF crystals, which benefits applications in laser optics. One source of the improved crystal growth is hydrogen bonding between lattice layers, which results from replacing potassium ions in KBBF with ammonium ions in ABF.—MITCH JACOBY



$NH_4B_4O_6F$ is a promising new Be-free NLO material for applications in the deep-UV range (< 200 nm); N is gray, H is white, B is blue, O is red, F is black.

…promises to further “break down the DUV wall for NLO materials”

C&EN, 2017, 95(11), 10； ***C&EN***, 2017, 95(33), 12.

Fluorooxoborate NLO crystals have received considerable attention

The discovery of ABF crystal was rewarded “Top 10 Breakthroughs in China Optics”

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中科院潘世烈团队：氟化硼酸盐体系探索深紫外非线性光学晶体材料

nanoyuhan 2个月前

【引言】

非线性光学(NLO)晶体是一
发展的关键材料之一。自
扩展了固态激光器的输出
源、工业制造和医疗卫生
磷酸二氢钾（KDP）、磷
（AGS）等，已经发展成
随着激光精密机械加工业
要发展全固态深紫外相干

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Researchers Synthesize Alkali Metal Flourooxoborate Deep-UV Nonlinear Optical Crystal

Nov 09, 2017 Email Print Text Size A A Share

As the key devices of the deep-ultraviolet (DUV, wavelength below 200 nm) all-solid-state lasers, DUV nonlinear optical (NLO) crystals have attracted increasing attention over the past decades.

$KBe_2BO_3F_2$ (KBBF) is the unique crystal that can directly generate the sixth harmonic laser of Nd: YAG lasers (wavelength = 177.3 nm). With excellent optical performances, KBBF crystal's intrinsic drawbacks like toxicity and layered growth habit limit the commercial applications. Thus, the design and synthesis of new DUV NLO crystal is of urgent demand.

面向世界科技前沿，面向国家重大需求，面向国民经济主战场，率先实现率先建成国家创新人才高地，率先建成国家高水平科技智库，率先建设国际一

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首页 > 科研进展

新疆理化所深紫外非线性光学晶体材料研究获进展

文章来源：新疆理化技术研究所 发布时间：2018-05-04 【字号： 小 中 大 】 我要分享

非线性光学晶体材料是重要的光电信息功能材料，在激光医学、激光频率变换、信息通讯、精密仪
等众多领域都具有重要应用。随着科技的发展，现阶段对非线性光学晶体材料提出了更高的要求。作为
激光器输出深紫外激光的关键元件，深紫外非线性光学晶体的研制和应用亟待发展突破。

中国科学院新疆理化技术研究所特殊环境功能材料与器件重点实验室潘世烈团队通过结构调控和组

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率先建成国家创新人才高地，率先建成国家高水平科技智库，率先建设国际一

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首页 > 科研进展

新疆理化所合成新型氟化硼酸盐深紫外非线性光学晶体

文章来源：新疆理化技术研究所 发布时间：2018-05-07 【字号： 小 中 大 】 我要分享

非线性光学晶体是一种重要的光电信息功能材料，是固体激光技术和光通讯与信号处理技术发展的关键材
料之一，随着激光精密机械加工业、激光化学、紫外激光光谱学和激光医学等学科的飞速发展，人们迫切需要
发展全固态深紫外相干光源，其关键突破点在于深紫外波段的非线性光学晶体的研制和应用。

中国科学院新疆理化技术研究所中科院特殊环境功能材料与器件重点实验室潘世烈团队，建立典型非线性
光学晶体材料的结构数据库，分析硼酸盐晶体“深紫外通过-大倍频效应-较大双折射”性能之间相互制约的原
因，基于材料模拟方法提出了一种将一类$BO_{3-x}F_x$ ($x=1, 2, 3$) 功能基团引入硼酸盐框架的设计策略，成功设计
了系列新型氟化硼酸盐深紫外非线性光学晶体，如LBOF、ABF和CBF。

近日，基于离子结构调控策略，潘世烈团队又合成一系列新型碱金属氟化硼酸盐非线性光学晶体材料，

潘世烈课题组：新一代深紫外非线性光学晶体材料

2017-09-28 16:34 设计

中科院新疆理化所潘世烈团队基于材料模拟方法提出了一种将(BO3F)4-功能基团引入硼酸盐框架的设计策略。成功设计并合成出了NH4B4O6F (ABF)块状晶体，倍频效应是KBBF的2.5倍，用于深紫外激光光源可获得更高的转换效率。

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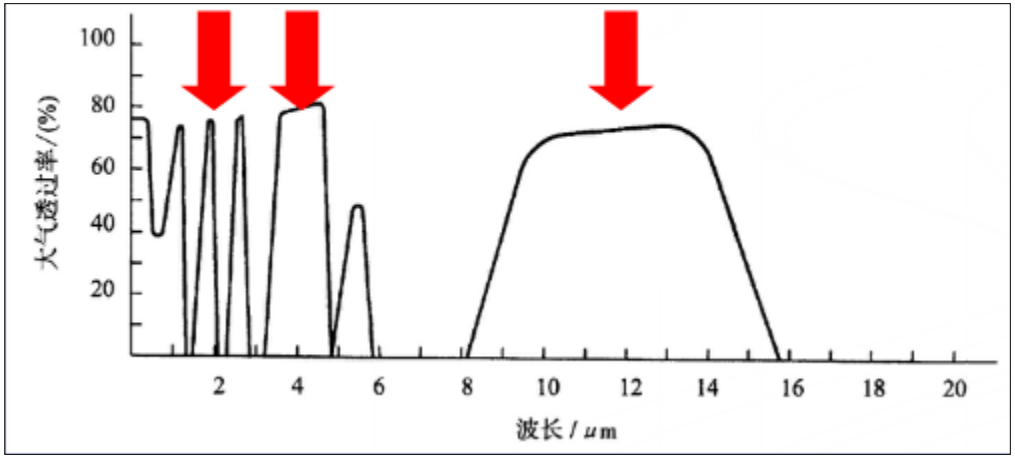
2.6 Mid-IR NLO crystal

Mid-IR laser: Wavelength range from 3 to 20 μm

Widely used in IR detector, medical treatment, spectral analysis, and military applications

- **Only a few IR NLO materials cover two important atmospheric transparent windows （3~5 μm， 8~14 μm）**



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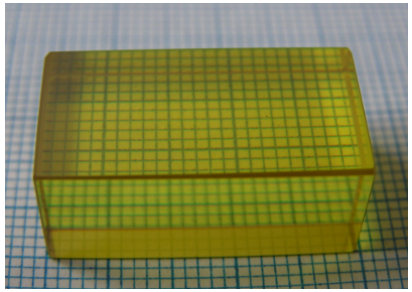
2.6 Mid-IR NLO crystal

Commercially available: $ZnGeP_2$, $AgGaS_2$ and $AgGaSe_2$

However, they suffer from two main drawbacks, including:

a. low laser damage thresholds (LDTs)

b. difficulty in growing high-quality crystals



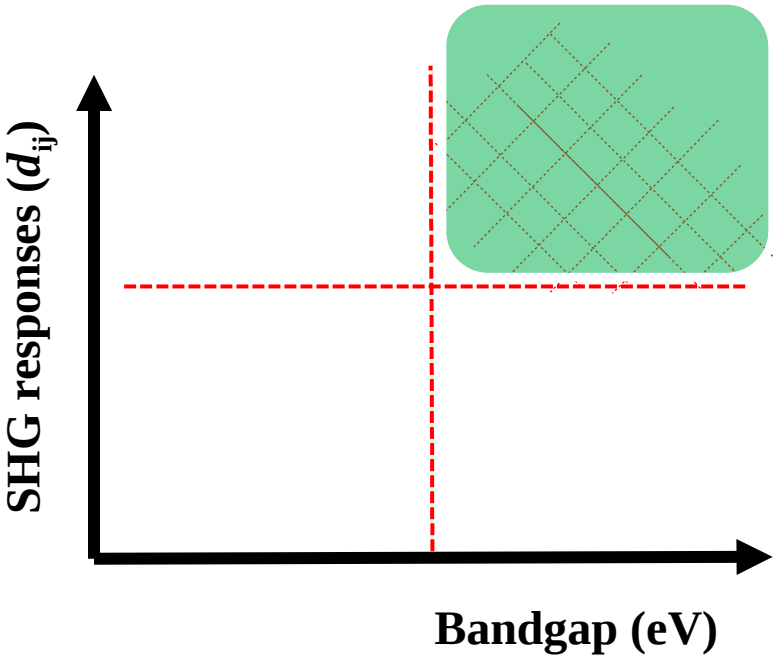
Therefore, the search for new IR NLO crystals with both high LDTs and moderate SHG responses that can also be easily grown is still a challenge in this field

2. Main Research Results

2.6.1 New Mid-IR NLO crystals

A high LDTs value strongly depends on the material having a large bandgap.

Thus, a good IR NLO material should demonstrate a critical balance between Bandgap (Eg> 3.0 eV) and SHG responses (d_{ij}> 10 × KDP)



New IR NLO materials

Strategy: alkaline/alkaline-earth cations and easily distorted MQ_4 ligands (M=Ga, In, Ge, Sn; Q=S, Se)

$Na_2ZnGe_2S_6$

Na_2BaMQ_4 (M=Ge, Sn; Q=S, Se)

$Na_2Hg_3M_2S_8$ (M = Si, Ge, and Sn)

2. Main Research Results

2.6.1 New Mid-IR NLO crystals

- New IR NLO materials with good balance
- between large SHG response and high LDTs

Materials	d_{ij} (× KDP)	Eg (eV)	LDTs (× $AgGaS_2$)
$Na_2ZnGe_2S_6$	30	3.25	6
Na_2BaSnS_4	17	3.27	
Na_2BaGeS_4	10	3.7	
$Na_2Hg_3Si_2S_8$	43	2.86	4.5
$Na_2Hg_3Ge_2S_8$	73	2.68	2.2
$Na_2Hg_3Sn_2S_8$	92	2.45	1

Guangmao Li, Zhihua Yang, Shilie Pan*, et al, *J. Am. Chem. Soc.* 2016, *138*, 7422.

Kui Wu, Zhihua Yang, Shilie Pan*, et al, *Angew. Chem. Int. Ed.*2016, *55*, 6713.

Kui Wu, Zhihua Yang, Shilie Pan*, et al, *J. Am. Chem. Soc.*, 2017, *139*, 14885.

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2.6.2 POC----Another Promising IR NLO material

Design strategy

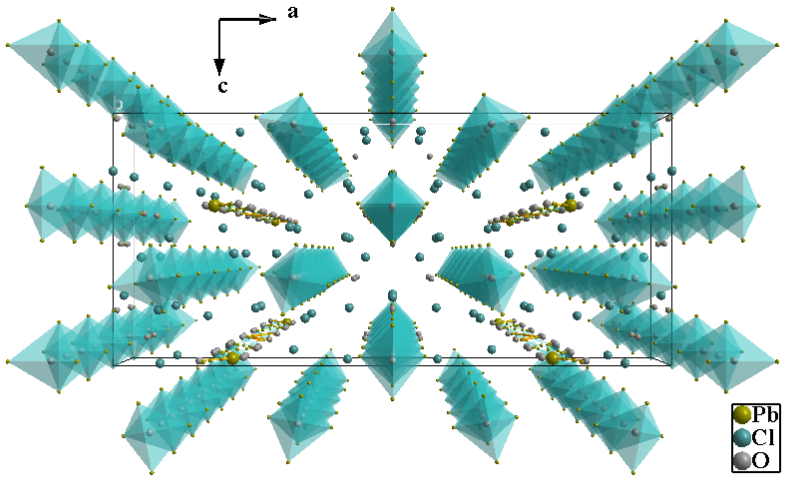
1. highly electronegative halide

A high LDT corresponds to a large energy band gap, which could be attained by anions to form strong ionic bonds

2. Pb^{2+} with lone-pair effect

second-order Jahn−Teller (SOJT) can produce large SHG response

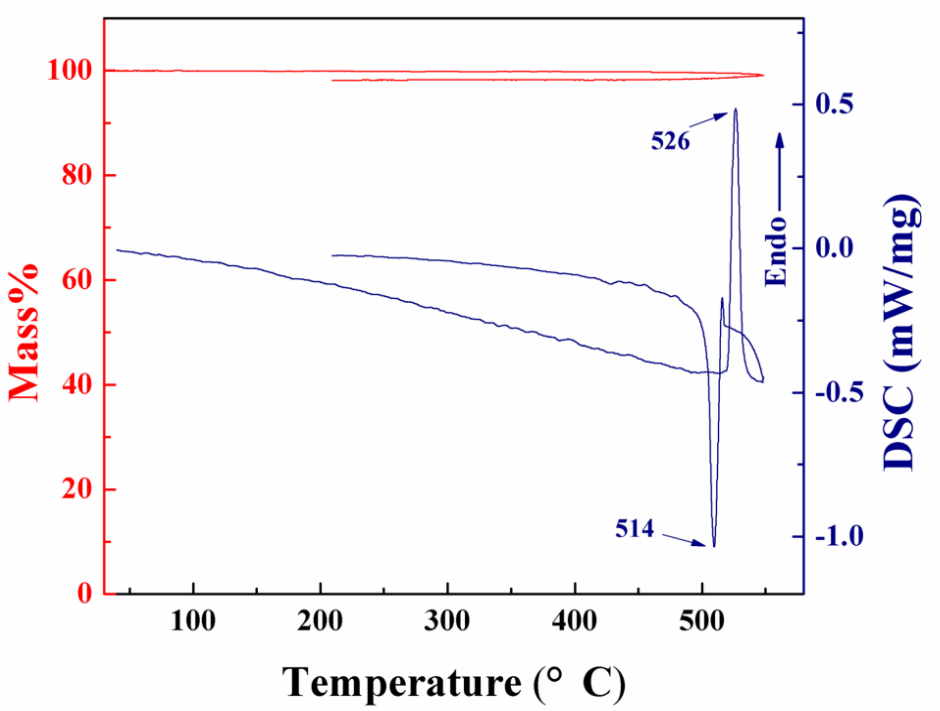
Pb-O has no absorption in mid-IR



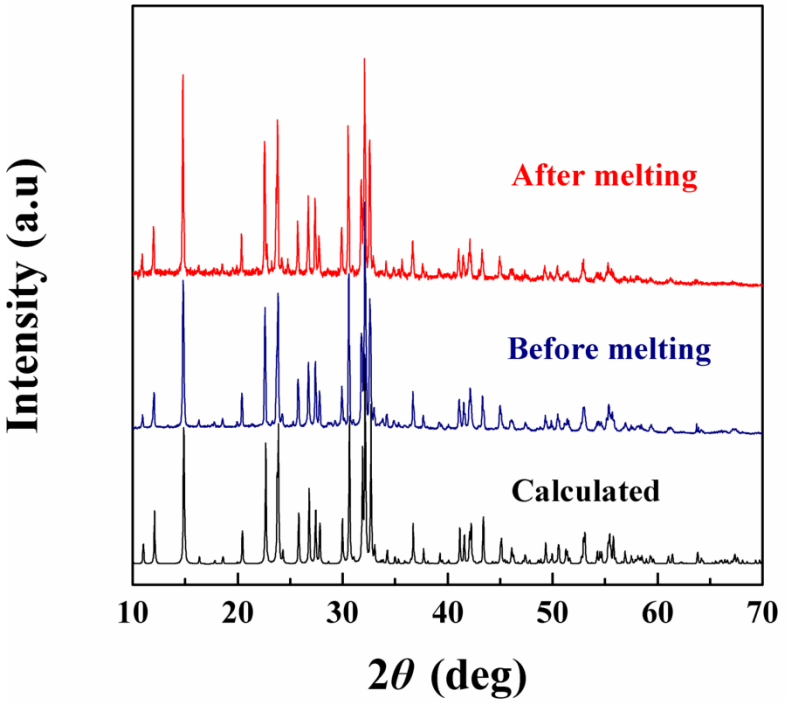
Crystal structure of $Pb_{17}O_8Cl_{18}$ （POC）

2. Main Research Results

2.6.2 POC---- thermal analysis



TG-DSC



XRD patterns

- Congruent melting behavior (m.p: 526 ℃) , thermally stable

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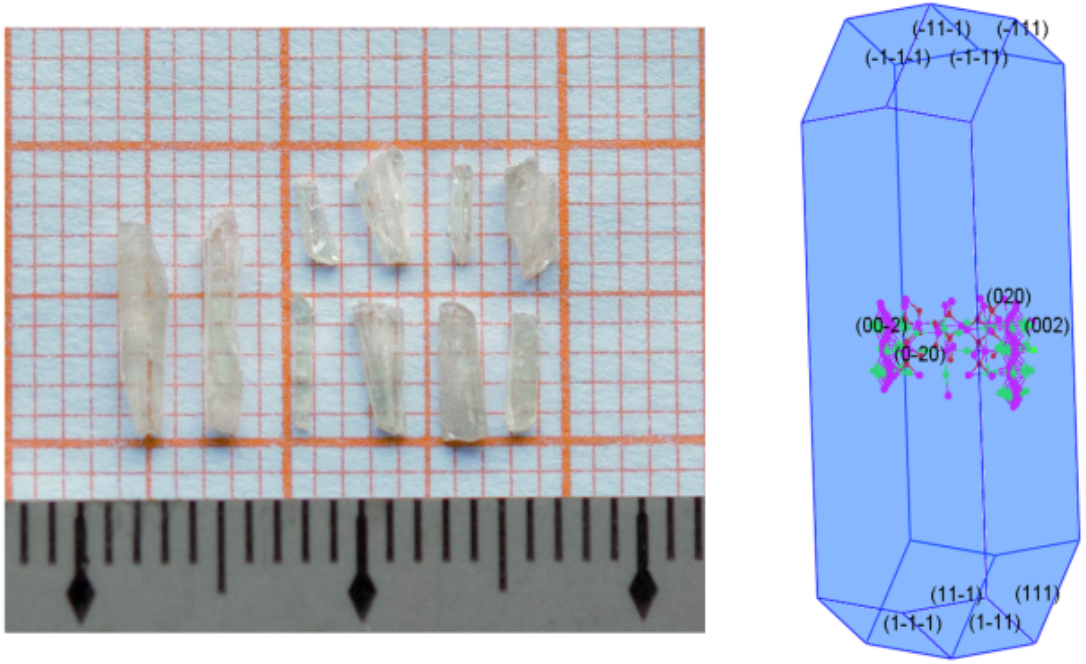
2.6.2 POC---- crystal growth

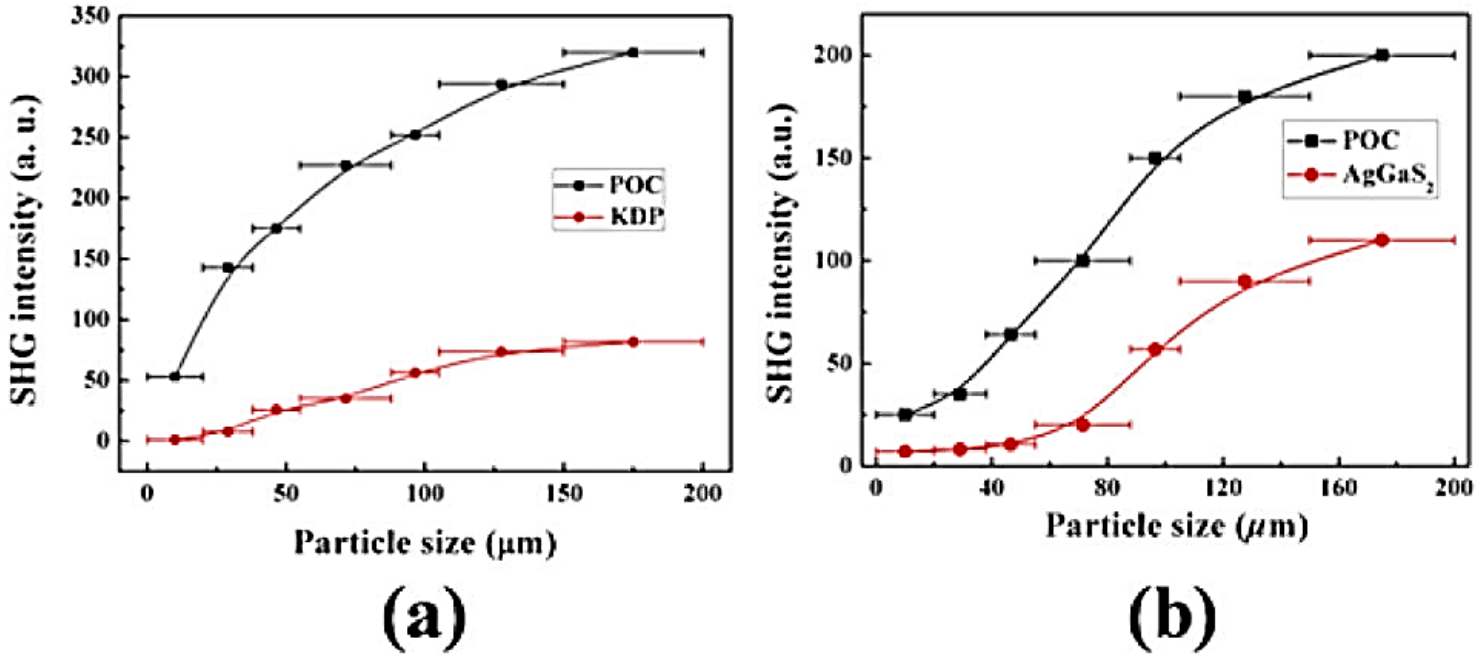


(a) (b)

POC single crystal

- **POC could be grown from its stoichiometric melt in the open system.**

2.6.2 POC---- SHG measurement

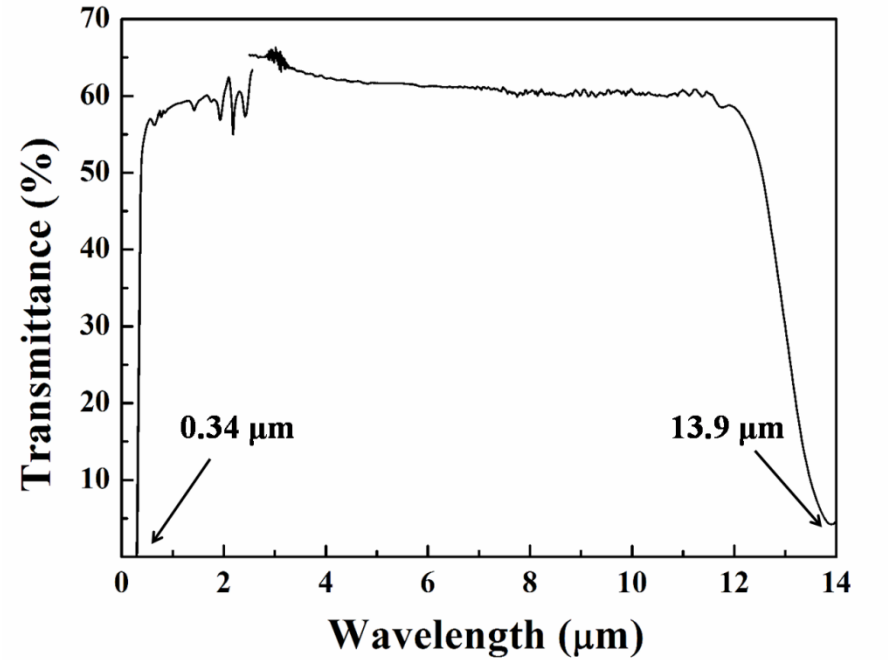


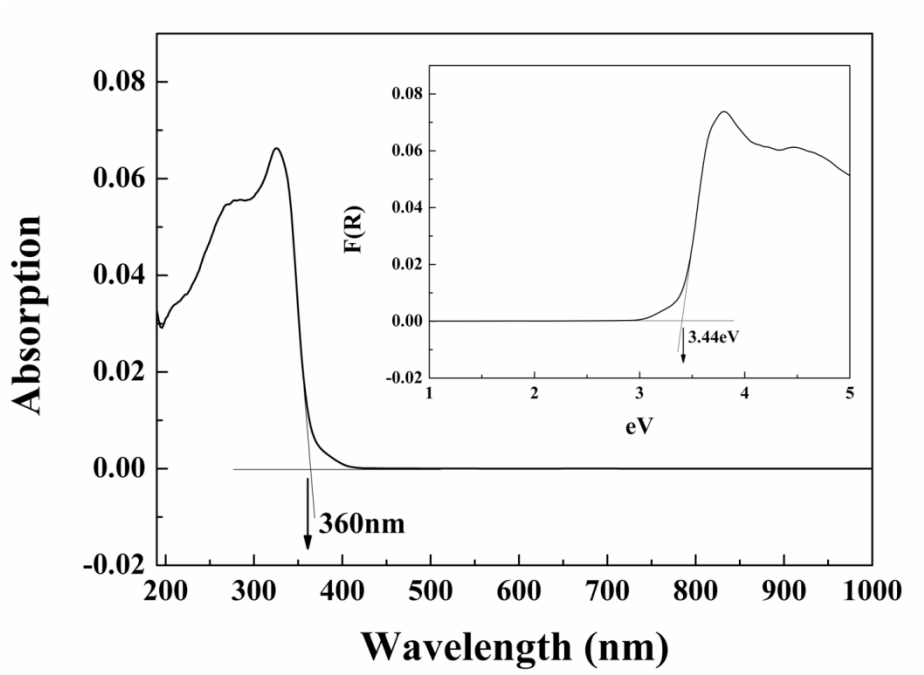
Phase-matching curves for POC at (a) 1064 nm and (b) 2090 nm

POC exhibits a large SHG response:

4 times that of KDP at 1064 nm and 2 times that of $AgGaS_2$ at 2090 nm

2.6.2 POC---- optical properties



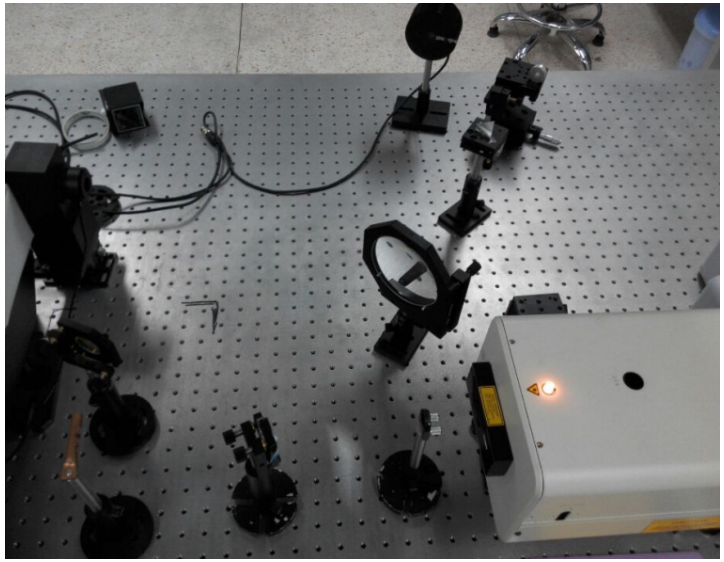


Transmittance spectra of POC.

- **POC is transparent over a broad spectral range from 0.34 to 13.9 μm**
- **It covers two important atmospheric transparent windows (3−5 and 8−14 μm) for optical applications**

2. Main Research Results

2.6.2 POC---- LDT test



LDT Measurement of POC with $AgGaS_2$ as the Reference

	damage energy (mJ)	spot diameter (mm)	LDT (MW/cm^2)
POC	2.01	0.25	408
$AgGaS_2$	0.35	0.375	32

- POC exhibits a large LDT value of 408 MW/cm^2 (1064 nm, 10 ns, 10 Hz).
- The LDT of POC is 12.8 times that of $AgGaS_2$

2.6.2 POC---- conclusion

- **POC exhibits a large LDT value of 408 MW/cm^2 (1064 nm, 10 ns, 10 Hz)**

- **Large LDT of 408 MW/cm^2, 12.8 times that of $AgGaS_2$.**

- **Excellent SHG response: 2 times that of $AgGaS_2$, the benchmark IR NLO crystal at 2090 nm, and 4 times that of KDP, the standard UV NLO crystal at 1064 nm.**

Thus, we believe that POC is a promising IR NLO material

Hui Zhang, Zhihua Yang, Shilie Pan*, et al, *J. Am. Chem. Soc.*, 2015, *137*, 8360.

2. Main Research Results

Summary

- We proposed new functional units: $BO_{4-x}F_x$ (x = 1 ~ 3) for new NLO materials
- ABF family are promising DUV NLO crystals
- Developing a new promising IR NLO material ---POC with large SHG effect & high LDT & wide transparent range

OUTLINE

1. Background

2. Main Research Results

3. **Further Work Plans**

- **Finding more possible DUV NLO crystals in fluorooxoborates system**

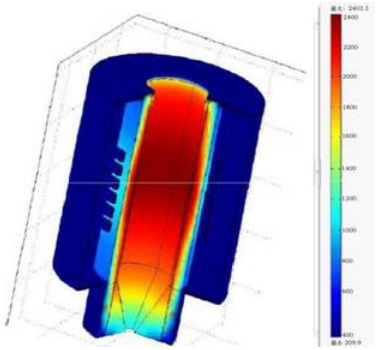
  Mixed alkali metal fluorooxoborates, CLBF, CKBF…

  The alkaline-earth metal fluorooxoborates, BaBOF, SrBOF…

- **Grow large crystals with high quality**

  Key issues: volatile fluorine element & high viscosity of the solution

  Solution: high temperature flux/solution method, suitable flux and thermal field



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2017.8.1

Thanks for your attention!

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- **Contact Email: slpan@ms.xjb.ac.cn (Shilie PAN)**

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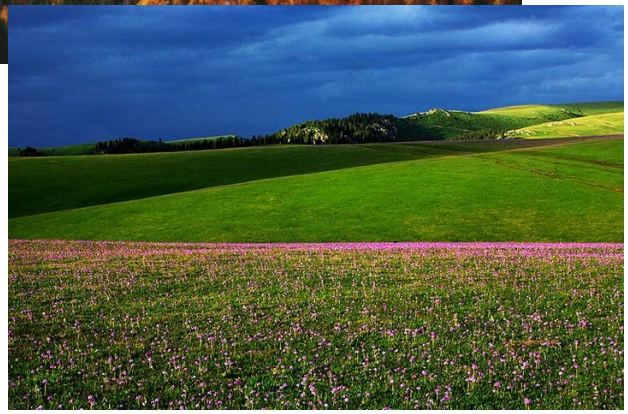

2.5 Fluorooxoborates: MB_4O_6F family

- MB_4O_6F family crystals are promising DUV NLO materials

Crystal	Cutoff edge (nm)	Birefringence@532nm	Shortest type I SHG wavelength (nm)*	Frequency-doubling coefficient (pm/V) *	Notes
KBBF	147	0.08	162	d_{11} = 0.47	Toxic raw material, layered structure
ABF	156	0.12	158	d_{32} = 1.07	Non-toxic, without layered structure
CBF	155	0.11	171.6	d_{32} = − 0.92	Melts congruently, non-toxic, without layered structure

*Calculated

Rational Design and Synthesis of New Nonlinear Optical Materials

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