Rational Design and Synthesis
of New Nonlinear Optical Materials

Shilie PAN

Xinjiang Technical Institute of Physics & Chemistry
Chinese Academy of Sciences
E-mail: slpan@ms.xjb.ac.cn

05/06/2018 @Skolkovo Institute of Science and Technology, Moscow
We are here!
XTIPC, Urumqi

Map of China
Locations of provinces, autonomous regions and municipalities.
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\cite{1} invented the ruby (Cr$^{3+}$ : Al$_2$O$_3$) laser.
- The nonlinear optical (NLO) effect was first observed in 1961 by Franken\cite{2}.

Then the search for new NLO materials becomes the focus of research.

The experiment setup of frequency conversion

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

<table>
<thead>
<tr>
<th>(D)UV</th>
<th>visible</th>
<th>infrared</th>
</tr>
</thead>
<tbody>
<tr>
<td>CANNOT meet the demand</td>
<td>meet basic needs</td>
<td>laser-induced damage threshold (LIDT) need to be improved</td>
</tr>
<tr>
<td>Large SHG Response</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Short Cut-off Edge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High laser-damaged threshold</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

...
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.

1. Background

1.6 Crucial requirements for DUV NLO materials

Balance of “Bandgap-SHG-Birefringence”

- Cutoff edge < 200 nm
- SHG response > 1KDP
- Suitable birefringence for phase-matching
- Easy to grow crystals and do not contain toxic raw material

Three Key factors

Challenge
## 1. Background

### 1.7 Research strategies

<table>
<thead>
<tr>
<th>demands</th>
<th>strategies</th>
<th>examples</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large SHG</td>
<td>with Jahn-Teller cations</td>
<td>BiB$_3$O$_6$</td>
<td>large distortion and SHG</td>
<td>red-shift the cutoff edge</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pb$_2$B$_5$O$_9$I</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cutoff edge</td>
<td>introduce Be to remove BO$_3$ dangling bonds</td>
<td>KBBF family</td>
<td>shorter than 200 nm</td>
<td>toxic beryllium</td>
</tr>
<tr>
<td>birefringence</td>
<td>with $\pi$-conjugation BO$_3$, CO$_3$, and NO$_3$ units</td>
<td>KBBF ABCO$_3$F</td>
<td>Sufficient birefringence for phase-matching</td>
<td>strong layering tendency, difficult to grow</td>
</tr>
</tbody>
</table>

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

- 143 NCS
- 34 with Cutoff \( \leq 200 \text{ nm} \)
- 21
- 74 with SHG \( \geq 1\text{KDP} \)
## 2. Main Research Results

### 2.1 Based on previous findings on NLO crystals

<table>
<thead>
<tr>
<th>Band gap (eV)</th>
<th>Crystal Structure</th>
<th>Cutoff edge</th>
</tr>
</thead>
<tbody>
<tr>
<td>(7.03)</td>
<td>LiK$_2$PO$_4$</td>
<td>170 nm</td>
</tr>
<tr>
<td>(7.29)</td>
<td>Li$_3$AlSiO$_5$</td>
<td>170 nm</td>
</tr>
<tr>
<td></td>
<td>LiCs$_2$PO$_4$</td>
<td>&lt;174 nm</td>
</tr>
<tr>
<td>(6.05)</td>
<td>NBeBO</td>
<td>&lt;175 nm</td>
</tr>
<tr>
<td>(7.01)</td>
<td>XJIPC-15</td>
<td>175 nm</td>
</tr>
<tr>
<td>(6.8)</td>
<td>KPB$_2$(PO$_3$)$_5$</td>
<td>177 nm</td>
</tr>
<tr>
<td>(6.4)</td>
<td>K$_3$B$<em>6$O$</em>{10}$Cl</td>
<td>180 nm</td>
</tr>
<tr>
<td>(5.9)</td>
<td>K$_3$B$<em>6$O$</em>{10}$Br</td>
<td>182 nm</td>
</tr>
<tr>
<td>(5.5)</td>
<td>Sr$_2$B$_5$O$_9$(OH)·H$_2$O</td>
<td>&lt;174 nm</td>
</tr>
<tr>
<td>(6.1)</td>
<td>Li$_2$B$_6$O$_9$F$_2$</td>
<td>190 nm</td>
</tr>
<tr>
<td>(5.8)</td>
<td>K$_3$B$_3$O$_4$(OH)$_4$·2H$_2$O</td>
<td>&lt;176 nm</td>
</tr>
<tr>
<td>(6.08)</td>
<td>M$_3$B$<em>6$O$</em>{11}$F$_2$ (M= Sr, Ba)</td>
<td>&lt;176 nm</td>
</tr>
<tr>
<td>(5.87)</td>
<td>Sr$<em>4$B$</em>{10}$O$_{18}$(OH)$_2$·2H$_2$O</td>
<td>&lt;176 nm</td>
</tr>
<tr>
<td>(5.62)</td>
<td>Ba$_4$(BO$_3$)$_3$(SiO$_4$).Ba$_3$Cl</td>
<td>&lt;177 nm</td>
</tr>
<tr>
<td>(6.0)</td>
<td>Ba$_4$(BO$_3$)$_3$(SiO$_4$).Ba$_3$Br</td>
<td>&lt;177 nm</td>
</tr>
<tr>
<td></td>
<td>Ba$<em>4$B$</em>{11}$O$_{20}$F</td>
<td>&lt;177 nm</td>
</tr>
<tr>
<td>(4.96)</td>
<td>Li$_4$CsB$<em>5$O$</em>{10}$</td>
<td>&lt;200 nm</td>
</tr>
<tr>
<td>(4.13)</td>
<td>Cs$_3$Zn$_6$B$<em>9$O$</em>{21}$</td>
<td>near 200 nm</td>
</tr>
</tbody>
</table>
2. Main Research Results

2.1 Based on previous findings on NLO crystals

Structure-property relationship analysis

- With $\pi$-conjugation
- Large SHG
- Pb-BO$_3$ connection
- Perovskite-like structure
- Short Cutoff edge
- Suitable birefringence
- Preferred orientation
- Tetrahedral units

Remove dangling bonds
2. Main Research Results

2.2 Choosing the suitable system

Borate halide might be an appropriate choice

SHG (×KDP)

Band gap (eV)
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.

![Diagram showing metal borate halides and probability of NCS structure]

Elsevier Book chapter focusing on F-containing metal borates.

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 KBF₄, LiB₆O₉F, Na₂B₆O₉F₂, 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

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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.

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.

Indirect contribution: polar displacement, producing large distortion

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

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: \( \text{BO}_{4-x}F_x \) (\( x = 1 \sim \))

Dipole moment (\( P \)), polarizability anisotropy (\( \delta \)), hyperpolarizability (\( |\beta_{\text{max}}| \)) and HUMO-LUMO gap.

| units               | \( P_x \), \( P_y \), \( P_z \) | (\( E_g \)) | \( |\beta_{\text{max}}| \) | \( E_g \) (eV) |
|--------------------|-----------------|------------|----------------|-------------|
| \( \text{BO}_3F^4^- \) | 2.2, 0.0, 0.0    | 2.1        | 39.5           | 9.7         |
| \( \text{BO}_2F_2^3^- \) | 0.0, 0.0, -2.3  | 3.4        | 82.6           | 9.2         |
| \( \text{BOF}_3^2^- \) | -1.8, 0.0, 0.0  | 2.5        | 30.9           | 9.5         |
| \( \text{BO}_4^5^- \) | 0.0, 0.0, 0.0   | 0.0        | 4.1            | 10.7        |
| \( \text{BO}_3^3^- \) | 0.0, 0.0, 0.0   | 7.1        | 10.8           | 8.5         |

DFT calculations reveal that \( \text{BO}_3F^4^- \), \( \text{BO}_2F_2^3^- \) and \( \text{BOF}_3^2^- \) units have a very large polarizability anisotropy and hyperpolarizability.

2. Main Research Results

2.3 New strategy for designing DUV NLO materials

- No d-d electron transitions in the UV region (high transmittance)
- Large band gap, low two-photon absorption and high laser-induced damage threshold
- \( \pi \) -conjugated planar BO\(_3\) is beneficial for large SHG response & moderate birefringence
- 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: $\text{Li}_2\text{B}_6\text{O}_9\text{F}_2$

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

Introducing of the F atoms “cut through” the fixed 3D B–O network of LBO
2. Main Research Results

2.4 Fluorooxoborates: Li$_2$B$_6$O$_9$F$_2$

- The suitable candidate: Li$_2$B$_6$O$_9$F$_2$
- 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

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

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$_4$B$_4$O$_6$F (ABF) (Space group $Pna2_1$, $a = 7.602$ Å, $b = 11.197$ Å, $c = 6.5952$ Å)

Superior to KBBF in two other aspects:
- Half of interlayer spacing---improved growth habit
- Doubled BO$_3$ density---larger SHG response
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

\[ n_x^2 = 2.10333 + \frac{0.00710}{\lambda^2} - 0.01094 \lambda^2 - 0.00909 \lambda^2 \]
\[ n_y^2 = 2.45077 + \frac{0.01058}{\lambda^2} - 0.02000 \lambda^2 \]
\[ n_z^2 = 2.47210 + \frac{0.01139}{\lambda^2} - 0.02130 \lambda^2 \]

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

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

Apply for Chinese and US Patents
2. Main Research Results

2.5 Fluorooxoborates: CBF

Example 2: CsB$_4$O$_6$F (CBF) (Space group $Pna2_1$, BUT shows a different structure)

[B$_4$O$_6$F] group, which is composed of three BO$_3$ triangles forming B$_3$O$_6$ rings and one BO$_3$F tetrahedron

Like KBBF, it features a two-dimensional (2D) [B$_4$O$_6$F]$_\infty$ anionic layer with the Cs$^+$ cations residing between the layers
2. Main Research Results

2.5 Fluorooxoborates: CBF

CBF inherits the excellent 
*genes* of \( \beta \)-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


Apply for Chinese and US Patents
2. Main Research Results

2.5 Fluorooxoborates: RBF/CKBF/CRBF

- Three new alkali metal fluorooxoborates were successfully synthesized

- By judicious selection of the A-site alkali metal cation, they show similar but different structures (space group: \textit{Pna2}_1, \textit{P321} and \textit{P}-\textit{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

\begin{align*}
\text{RbB}_4\text{O}_6\text{F} & \text{ (RBF)} \\
\text{CsKB}_8\text{O}_{12}\text{F}_2 & \text{ (CKBF)} \\
\text{CsRbB}_8\text{O}_{12}\text{F}_2 & \text{ (CRBF)}
\end{align*}

2. Main Research Results

2.5 Fluorooxoborates: NBF

Sodium Fluorooxoborate crystallizes in space group C2 and NaB₄O₆F exhibits outstanding NLO properties.

Suitable SHG response (0.9 × KDP)
Shortest type I phase-matching wavelength (~166 nm)

2. Main Research Results

2.5 Fluorooxoborates: SBOF

The first case of NLO-active alkaline earth fluorooxoborates: SrB$_5$O$_7$F$_3$

SrB$_5$O$_7$F$_3$ 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$_5$O$_7$F$_3$ structure](image1.png)

![phase-matching condition](image2.png)

![B$_5$O$_9$F$_3$ double ring](image3.png)

2. Main Research Results

2.5 Fluorooxoborates: CBOF

- **CaB₅O₇F₃** UV cutoff edge <180 nm, SHG effect \(~2\times\text{KDP}\) (larger!), shortest phase-matching second harmonic wavelength \(~183\) nm
- The enhanced SHG response originates from the contributions of B₅O₉F₃ double rings and Ca²⁺ cations

![CaB₅O₇F₃ SHG density map](image)
## 2. Main Research Results

### 2.5 Fluorooxoborates: summary

Fluorooxoborate crystals are promising DUV NLO materials

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Absorption edge (nm) or band gap (eV)</th>
<th>SHG intensity (× KDP) @1064 nm</th>
<th>Shortest PM SHG wavelength (nm)</th>
<th>Feature</th>
</tr>
</thead>
<tbody>
<tr>
<td>KBBF</td>
<td>147 (8.43)</td>
<td>1.2</td>
<td>162</td>
<td>Toxic raw material, layered structure</td>
</tr>
<tr>
<td>LiB$_6$O$_9$F</td>
<td>(8.37)*</td>
<td>~</td>
<td>~</td>
<td></td>
</tr>
<tr>
<td>Li$_2$B$_6$O$_9$F$_2$</td>
<td>(8.05)*</td>
<td>0.9</td>
<td>192</td>
<td></td>
</tr>
<tr>
<td>Li$_2$B$_3$O$_4$F$_3$</td>
<td>(8.42)*</td>
<td>~</td>
<td>~</td>
<td></td>
</tr>
<tr>
<td>NH$_4$B$_4$O$_6$F</td>
<td>156 (7.95)</td>
<td>3.0</td>
<td>158</td>
<td></td>
</tr>
<tr>
<td>NaB$_4$O$_6$F</td>
<td>&lt;180 (166)*</td>
<td>0.9</td>
<td>166*</td>
<td>non-toxic, without layered tendency</td>
</tr>
<tr>
<td>RbB$_4$O$_6$F</td>
<td>&lt;200 (7.73)*</td>
<td>0.8</td>
<td>165*</td>
<td></td>
</tr>
<tr>
<td>CsB$_4$O$_6$F</td>
<td>155 (8.00)</td>
<td>1.9</td>
<td>172</td>
<td></td>
</tr>
<tr>
<td>CsKB$<em>8$O$</em>{12}$F$_2$</td>
<td>&lt;200 (7.76)*</td>
<td>1.9</td>
<td>170*</td>
<td></td>
</tr>
<tr>
<td>CsRbB$<em>8$O$</em>{12}$F$_2$</td>
<td>&lt;200</td>
<td>1.1</td>
<td>~</td>
<td></td>
</tr>
<tr>
<td>CaB$_5$O$_7$F$_3$</td>
<td>&lt;180 (8.75)*</td>
<td>2.0</td>
<td>183*</td>
<td></td>
</tr>
<tr>
<td>SrB$_5$O$_7$F$_3$</td>
<td>&lt;180 (8.58)*</td>
<td>1.6</td>
<td>180*</td>
<td></td>
</tr>
</tbody>
</table>

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

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 materials currently used (Angew. Chem. Int. Ed. 2017, DOI: 10.1002/anie.201700540). DUV NLO materials promises to further “break down the DUV wall for NLO 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). K(ReBO₃)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 Shilu Pan of Xinjiang Technical Institute of Physics & Chemistry and Kenneth R. Pueschelmeier of Northwestern University may have come up with a solution—NH₄BO₃F (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 KBF₄ with NH₄F, 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 JACKBY

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”
2. Main Research Results

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)
2. Main Research Results

2.6 Mid-IR NLO crystal

Commercially available: $\text{ZnGeP}_2$, $\text{AgGaS}_2$ and $\text{AgGaSe}_2$

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 ($d_{ij} > 10 \times \text{KDP}$).

New IR NLO materials

Strategy: alkaline/alkaline-earth cations and easily distorted MQ$_4$ ligands
(M=Ga, In, Ge, Sn; Q=S, Se)

- Na$_2$ZnGe$_2$S$_6$
- Na$_2$BaMQ$_4$ (M=Ge, Sn; Q=S, Se)
- Na$_2$Hg$_3$M$_2$S$_8$ (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

<table>
<thead>
<tr>
<th>Materials</th>
<th>$d_{ij}$ (× KDP)</th>
<th>$E_g$ (eV)</th>
<th>LDTs (× AgGaS$_2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$ZnGe$_2$S$_6$</td>
<td>30</td>
<td>3.25</td>
<td>6</td>
</tr>
<tr>
<td>Na$_2$BaSnS$_4$</td>
<td>17</td>
<td>3.27</td>
<td></td>
</tr>
<tr>
<td>Na$_2$BaGeS$_4$</td>
<td>10</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Na$_2$Hg$_3$Si$_2$S$_8$</td>
<td>43</td>
<td>2.86</td>
<td>4.5</td>
</tr>
<tr>
<td>Na$_2$Hg$_3$Ge$_2$S$_8$</td>
<td>73</td>
<td>2.68</td>
<td>2.2</td>
</tr>
<tr>
<td>Na$_2$Hg$_3$Sn$_2$S$_8$</td>
<td>92</td>
<td>2.45</td>
<td>1</td>
</tr>
</tbody>
</table>

2. Main Research Results

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$_8$Cl$_{18}$ (POC)
### 2. Main Research Results

#### 2.6.2 POC---- thermal analysis

**Congruent melting behavior (m.p: 526 °C), thermally stable**
2. Main Research Results

2.6.2 POC---- crystal growth

POC single crystal

- POC could be grown from its stoichiometric melt in the open system.
2. Main Research Results

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. Main Research Results

2.6.2 POC---- optical properties

- 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

POC exhibits a large LDT value of 408 MW/cm² (1064 nm, 10 ns, 10 Hz).

The LDT of POC is 12.8 times that of AgGaS₂.
2. Main Research Results

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.

2. Main Research Results

**Summary**

- We proposed **new functional units**: $\text{BO}_{4-x}\text{F}_x$ ($x = 1 \sim 3$) 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
Thanks for your attention!
Welcome to New Opto-electronic Functional Material Laboratory!

- Post-doc
- Phd, Exchange students
- Field: Physics, Chemistry, Material Science
- Contact Email: slpan@ms.xjb.ac.cn (Shilie PAN)

Join us!

- 6 Professors
- 6 Associate professors
- 1 Assistant professor
- 4 Postdoc (2 foreigners)
- 60+ Students (3 foreigners)

Funds & Fellowship
- National foundation
- Chinese Academy of Science
Welcome to XINJIANG/CHINA!
2. Main Research Results

### 2.5 Fluorooxoborates: MB$_4$O$_6$F family

- **MB$_4$O$_6$F family crystals are promising DUV NLO materials**

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

*Calculated*
Rational Design and Synthesis of New Nonlinear Optical Materials

Shilie PAN

Xinjiang Technical Institute of Physics & Chemistry, Chinese Academy of Sciences
40-1 South Beijing Road, Urumqi 830011, China
E-mail: slpan@ms.xjb.ac.cn

06/06/2018 @MSU, Moscow