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Growth of borate-based crystals for blue-UV laser generation by the micro-pulling down technique

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- studying suitable materials for frequency conversion in the blue-UV range
- growth of good optical quality fiber crystals by the micro-pulling down technique (µ-PD)

Interest of crystalline fibers: aspect ratio and heat dissipation

## Materials: borates

<table>
<thead>
<tr>
<th>Property</th>
<th>Bi₂Zn₂B₂O₇ (BZBO)</th>
<th>LaBGeO₃ (LBGO)</th>
<th>BaCa(OB)₃F (CBF)</th>
<th>Caₓ(BO₃)ₓF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hygroscopicity</td>
<td>No</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Congruent melting</td>
<td>Yes 692°C</td>
<td>Yes 725°C</td>
<td>Yes 1205°C</td>
<td>No 1277°C</td>
</tr>
<tr>
<td>SHG efficiency for λ = 1064 nm</td>
<td>1.4 times KDP (type I phase-matching (KX plane))</td>
<td>2 times KDP (type II phase-matching)</td>
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</tr>
<tr>
<td>UV absorption edge</td>
<td>350 nm</td>
<td>190 nm</td>
<td>190 nm</td>
<td>196 nm</td>
</tr>
<tr>
<td>Birefringence and optical axes</td>
<td>positive, biaxial</td>
<td>positive, uniaxial</td>
<td>negative, uniaxial</td>
<td>negative, biaxial</td>
</tr>
</tbody>
</table>

**BiZn₂B₂O₇ : BZBO**

Transparent and uniformly colored fiber (yellow-red) without cracks and bubbles

**DTA traces of BZBO crushed fibers**

- Bi-rich small clear parts of different shapes dispersed in a darker matrix
- Elementary analysis of BZBO crushed fibers
- B₁.₂₁Zn₁₂.₇₉O₁₈.₅₄

**Evaporation of B₂O₃ (13.5%)**

- Incongruent behavior of the melt (peritectic type?)
- Growth with low pulling rate: 0.15 mm h⁻¹
- Colorless crystal

**BaCaBO₃F : CBF**

BCF fiber and SEM characterization of fibers obtained

<table>
<thead>
<tr>
<th>V = 12 mm h⁻¹</th>
<th>V = 4.2 mm h⁻¹</th>
<th>V = 2.4 mm h⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Black, opaque fiber</td>
<td>Colored, quasi transparent fiber</td>
<td>Colored, opaque fiber</td>
</tr>
</tbody>
</table>

- Presence of different phases and cracks

**EDS characterization:** presence of Pt and Rh

- µ-PD is not a suitable method for BCBF fiber growth

## Crystal growth by µ-PD

**LaBGeO₃ : LBGO**

Flux growth required

- Atmosphere: air
- Seed: platinum wire
- Pulling rates: 0.15 – 12 mm h⁻¹
- Fiber diameter: 50 µm to several mm

**LaBGeO₃**

- Homogeneous composition crystal
- High crystal quality
- Little feed material
- High pulling rate (up to 12 mm h⁻¹)

**Caₓ(BO₃)ₓF : CBF**

Flux growth: 70 wt% CBF, 22.5 wt% LiF, 7.5 wt% B₂O₃

Optimization of the growth conditions:

- Ratio capillary diameter/pulling rate
- Pulling rate: 3 mm h⁻¹
- Capillary diameter: 0.9–1.1 mm

**Caₓ(BO₃)ₓF**

- Growth conditions well defined. Good quality crystal fibers obtained
- Growth impossible by µ-PD

**LBGO : LiF-B₂O₃ flux needs to be improved and optimized to hope obtaining single-crystal fibers**

## Conclusions

Growth of borate-based crystals by µ-PD: not an easy task!

BZBO: growth of transparent and colorless crystals possible with a very low pulling rate.
CBF: growth conditions well defined. Good quality crystal fibers obtained
BCBF: growth impossible by µ-PD