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

Marianne Cochez, Michel Ferriol, Michel Aillerie

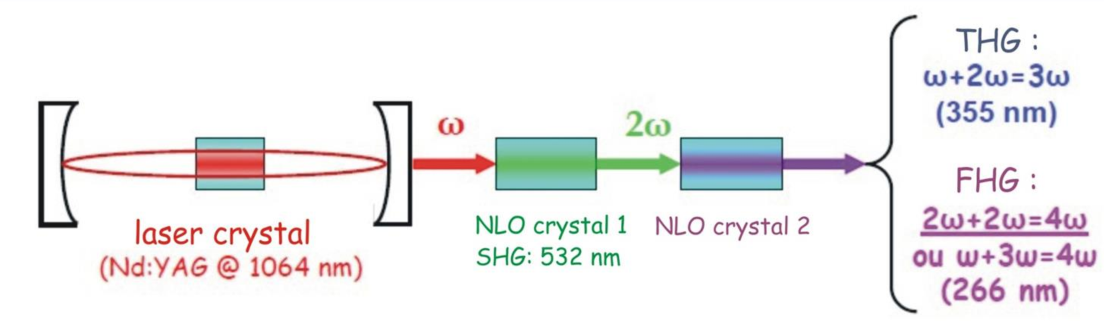
Growth of borate-based crystals for blue-UV laser generation by the micro-pulling down technique

Marianne COCHEZ, Michel FERRIOL, Michel AILLERIE
Université de Lorraine-CentraleSupélec, Laboratoire Matériaux Optiques, Photonique et Systèmes, Metz, France
marianne.cochez@univ-lorraine.fr

❶ Final goal

- 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

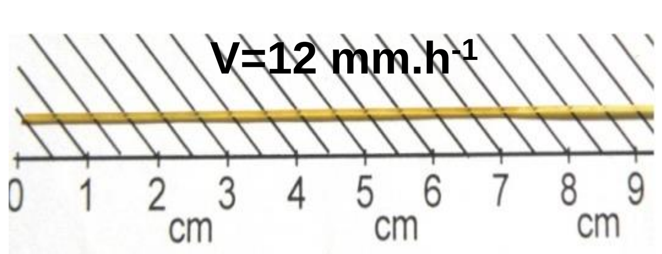


❷ Materials : borates

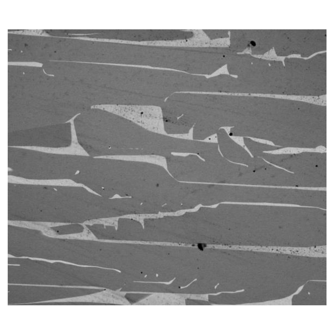
Property	$Bi_2ZnB_2O_7$ (BZBO)	$LaBGeO_5$ (LBGO)	$BaCaBO_3F$ (BCBF)	$Ca_5(BO_3)_3F$ (CBF)
Hygroscopicity	No	No	No	No
Congruent melting	Yes 692 °C	Yes 1205 °C	Yes 1090°C	No 1277 °C
SHG efficiency for l=1064 nm	≈four times KDP (type I phase-matching (XY plane))	one-two times KDP (type I phase-matching)	= KDP	two times KDP (type II phase-matching (XY plane))
UV absorption edge	350 nm	190 nm	190 nm	196 nm
Birefringence and optical axes	positive, biaxial	positive, uniaxial	negative, uniaxial	negative, biaxial

❹ $BiZn_2B_2O_7$: BZBO

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



SEM characterization



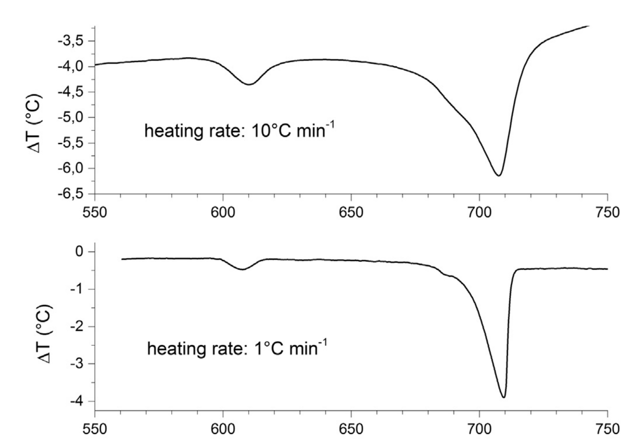
Bi-rich small clear parts of different shapes dispersed in a darker matrix

Elementary analysis of BZBO crushed fibers

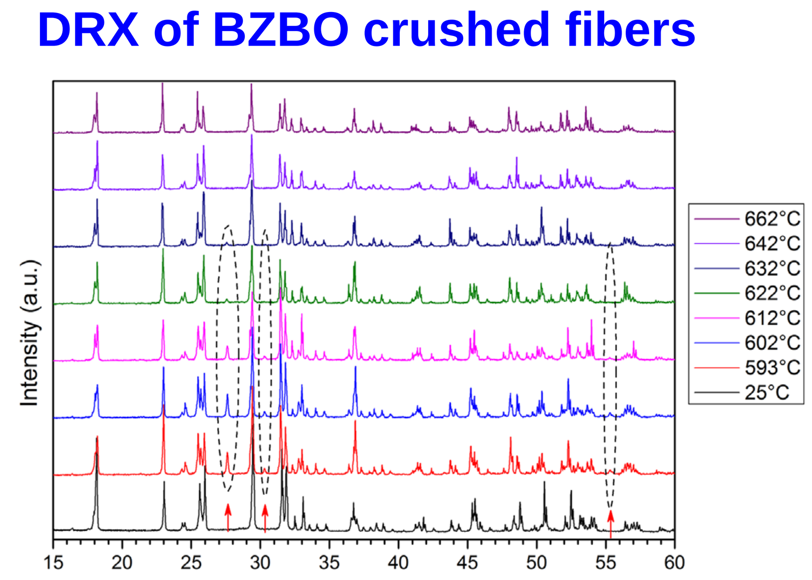
$Bi_{1,99}Zn_1B_{1,37}O_{6,54}$

Evaporation of B_2O_3 (13.5%)

DTA traces of BZBO crushed fibers



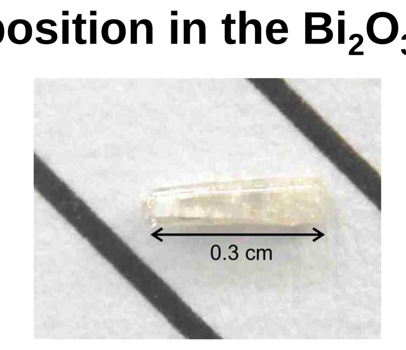
DRX of BZBO crushed fibers



Shift of the melt and crystal composition in the Bi_2O_3-B_2O_3-ZnO

Incongruent behavior of the melt (peritectic type?)

Growth with low pulling rate : 0,15 mm.h-1

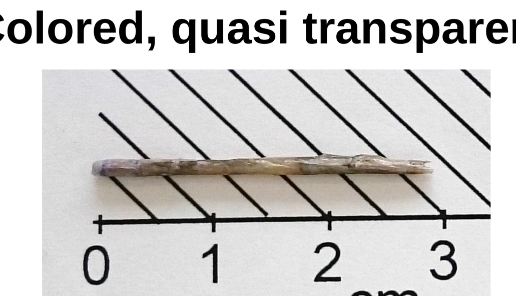


Colorless crystal

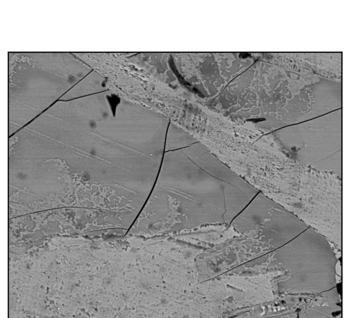
❺ $BaCaBO_3F$: BCBF

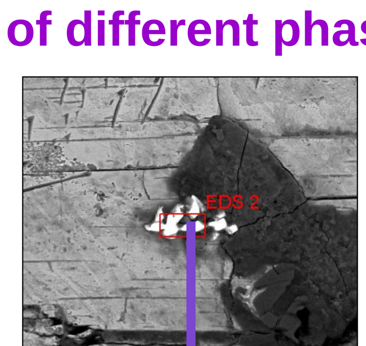
BCBF fiber and SEM characterization of fibers obtained

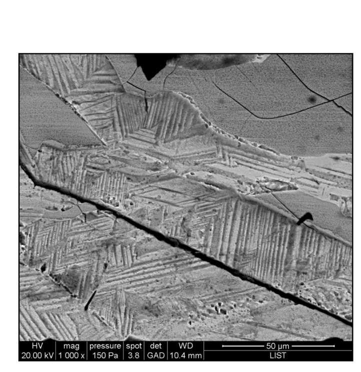
V = 12 mm.h-1	V = 4.2 mm.h-1	V = 2.4 mm.h-1
Black, opaque fiber	Colored, quasi transparent fiber	Colored, opaque fiber



Presence of different phases and cracks





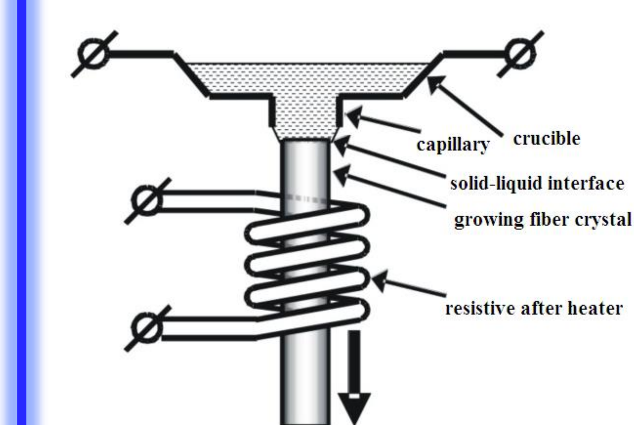


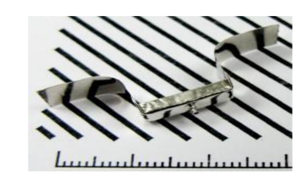
EDS characterization : presence of Pt and Rh

⇒ reaction of the melt with crucible

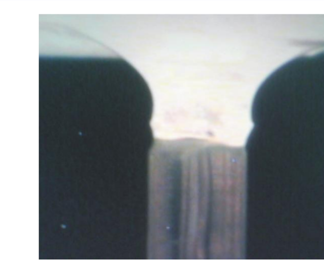
µ-PD is not a suitable method for BCBF fiber growth

❸ Crystal growth by µ-PD





hand made Pt crucible



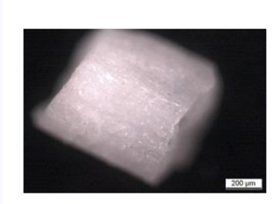
Interest of µ-PD:

- Homogeneous composition crystal
- High crystal quality
- Little feed material
- High pulling rate (up to 12 mm/h)
- Fiber diameter : 50 µm to several mm

Growth conditions:

- Atmosphere: air
- Seed: platinum wire
- Pulling rates: 0.15 – 12 mm.h-1
- Pt/Rh (95/5) or Pt crucible fitted with a capillary (0.7-1.2 mm internal diameter)

❻ $LaBGeO_5$: LBGO



V= 4.5 mm.h-1

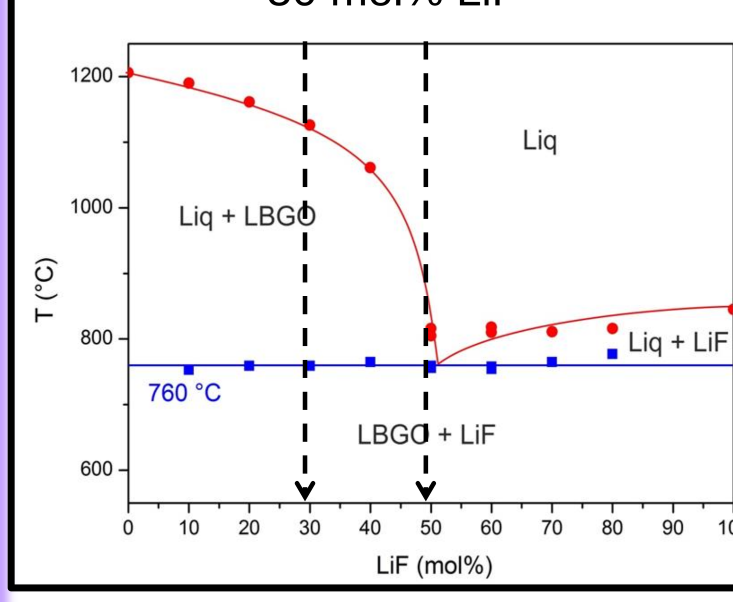
Too high viscosity → **Flux growth required**

Several fluxes tested :

- LiF
- LiF+B_2O_3
- ~~CaF_2~~
- ~~NaF-B_2O_3~~
- ~~$LiBO_2$~~
- ~~La_2O_3~~

LiF flux

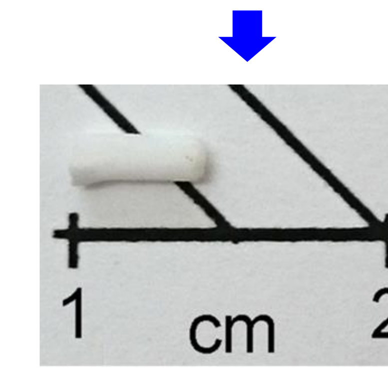
* 30 mol% LiF
* 50 mol% LiF



Failure of growth attempts due to :

- still too high viscosity
- strong LiF evaporation

* 80 mol% LiF



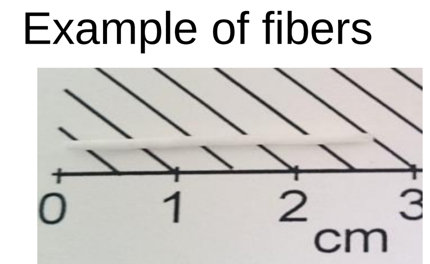
LBGO polycrystalline fiber confirmed by Raman spectroscopy

LiF+B_2O_3 flux

Addition of B_2O_3 in order to decrease LiF evaporation

Flux composition (mol %)	Result of growth trial	Remarks
LBGO 60%-LiF 30%-B_2O_3 10%	failure	melt too viscous
LBGO 50%-LiF 40%-B_2O_3 10%	failure	melt too viscous
LBGO 40%-LiF 50%-B_2O_3 10%	success (1 to 4 cm)	polycrystalline
LBGO 63%-LiF 50%-B_2O_3 7%	success (1 to 4 cm)	polycrystalline

Example of fibers



Polycrystalline fiber
Raman spectroscopy shows the presence of an unidentified phase

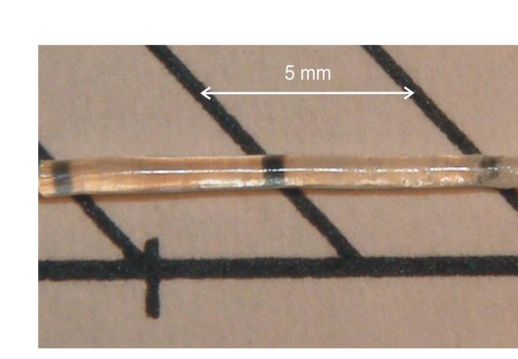
❼ $Ca_5(BO_3)_3F$: CBF

Flux growth : 70 wt% CBF, 22.5 wt% LiF, 7.5 wt% B_2O_3

Optimization of the growth conditions :

Ratio capillary diameter/pulling rate

- **Pulling rate : 3 mm.h-1**
- **Capillary diameter : 0,9-1 mm**



Transparent fiber

❽ 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

LBGO: LiF-B_2O_3 flux needs to be improved and optimized to hope obtaining single-crystal fibers