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Marianne Cochez, Michel Ferriol, Michel Aillerie

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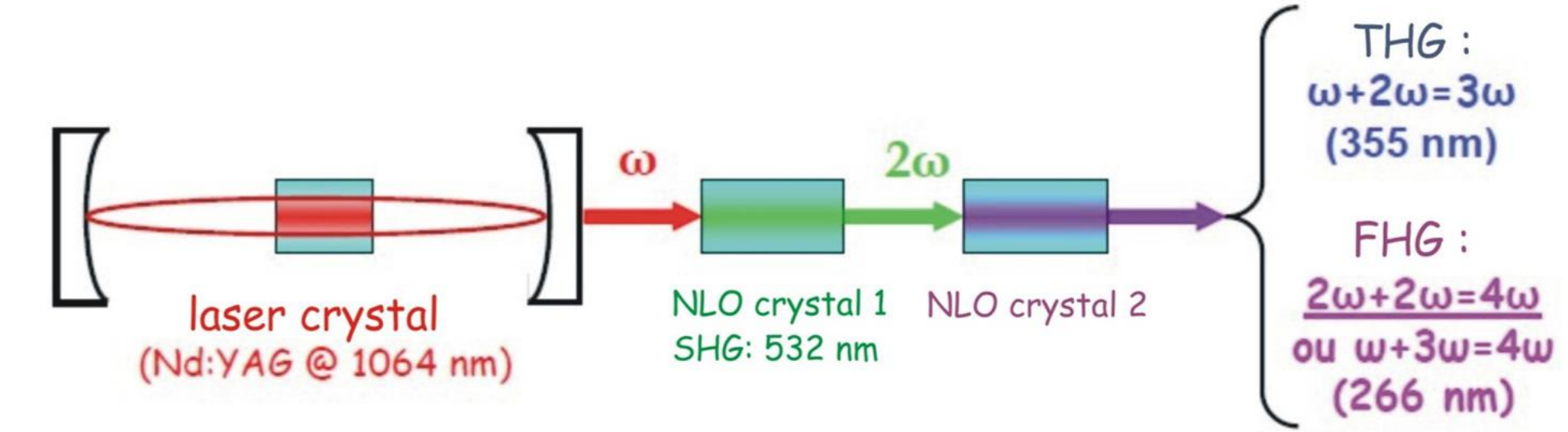
Growth of borate-based crystals for blue-UV laser generation by the micro-pulling down technique

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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

Final goal



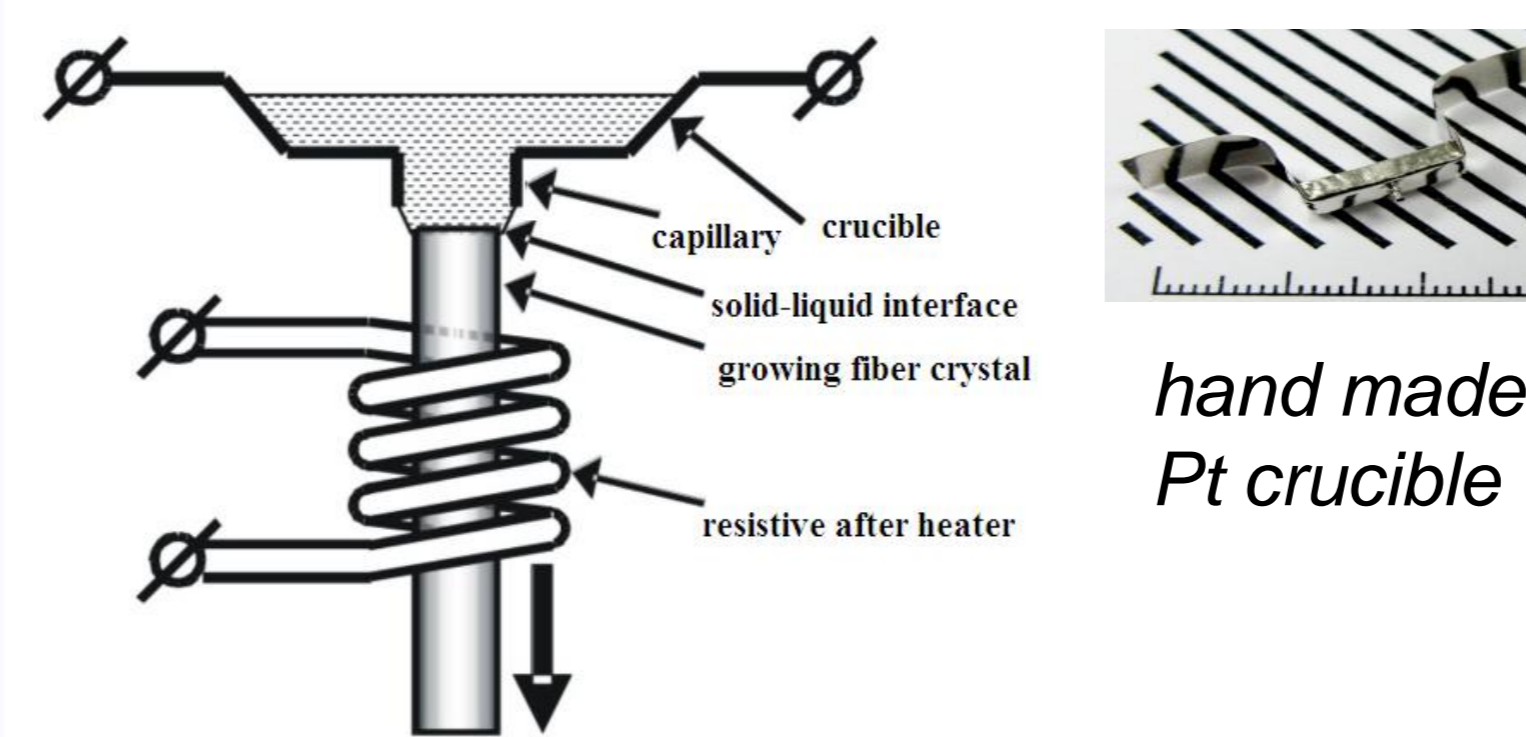
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Materials : borates

Property	Bi ₂ ZnB ₂ O ₇ (BZBO)	LaBGeO ₅ (LBGO)	BaCaBO ₃ F (BCBF)	Ca ₅ (BO ₃) ₃ F (CBF)
Hygroscopicity	No	No	No	No
Congruent melting	Yes 692 °C	Yes 1205 °C	Yes 1090°C	No 1277 °C
SHG efficiency for $\lambda=1064$ nm	\approx 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

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Crystal growth by μ -PD



Interest of μ -PD:

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

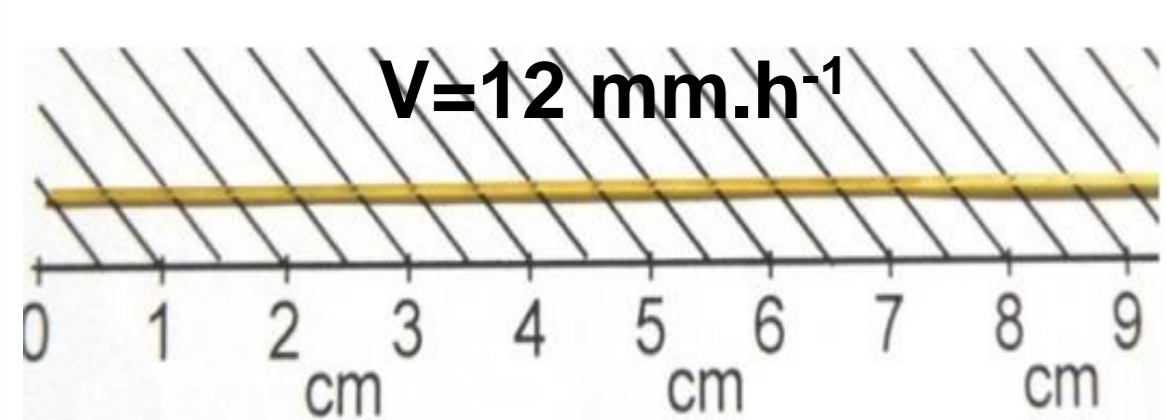
Growth conditions:

- 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)

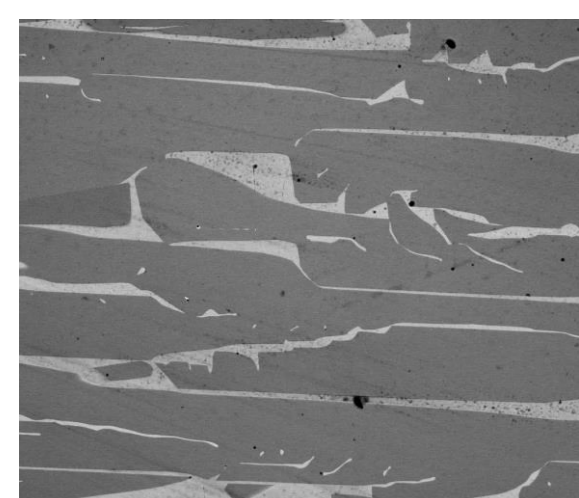
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BiZn₂B₂O₇ : BZBO

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

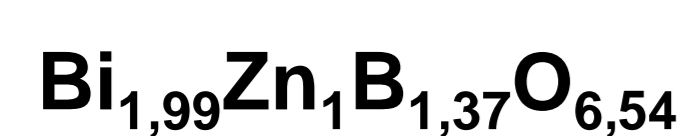


SEM characterization



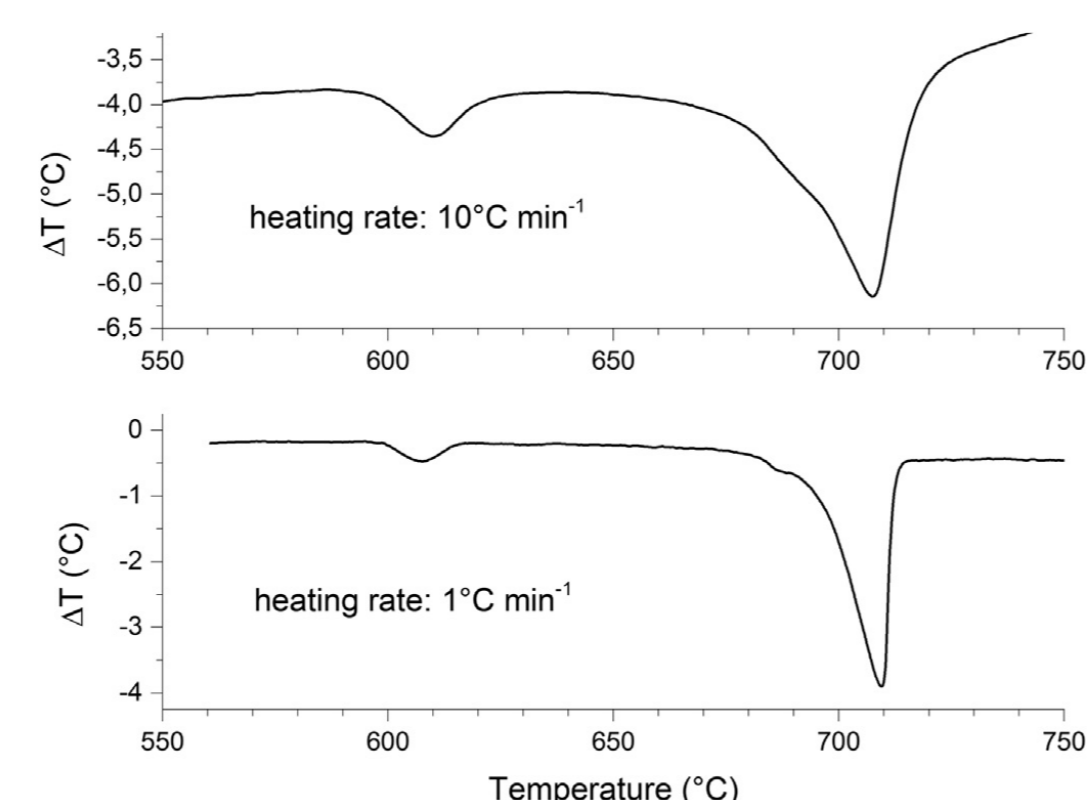
Bi-rich small clear parts of different shapes dispersed in a darker matrix

Elementary analysis of BZBO crushed fibers

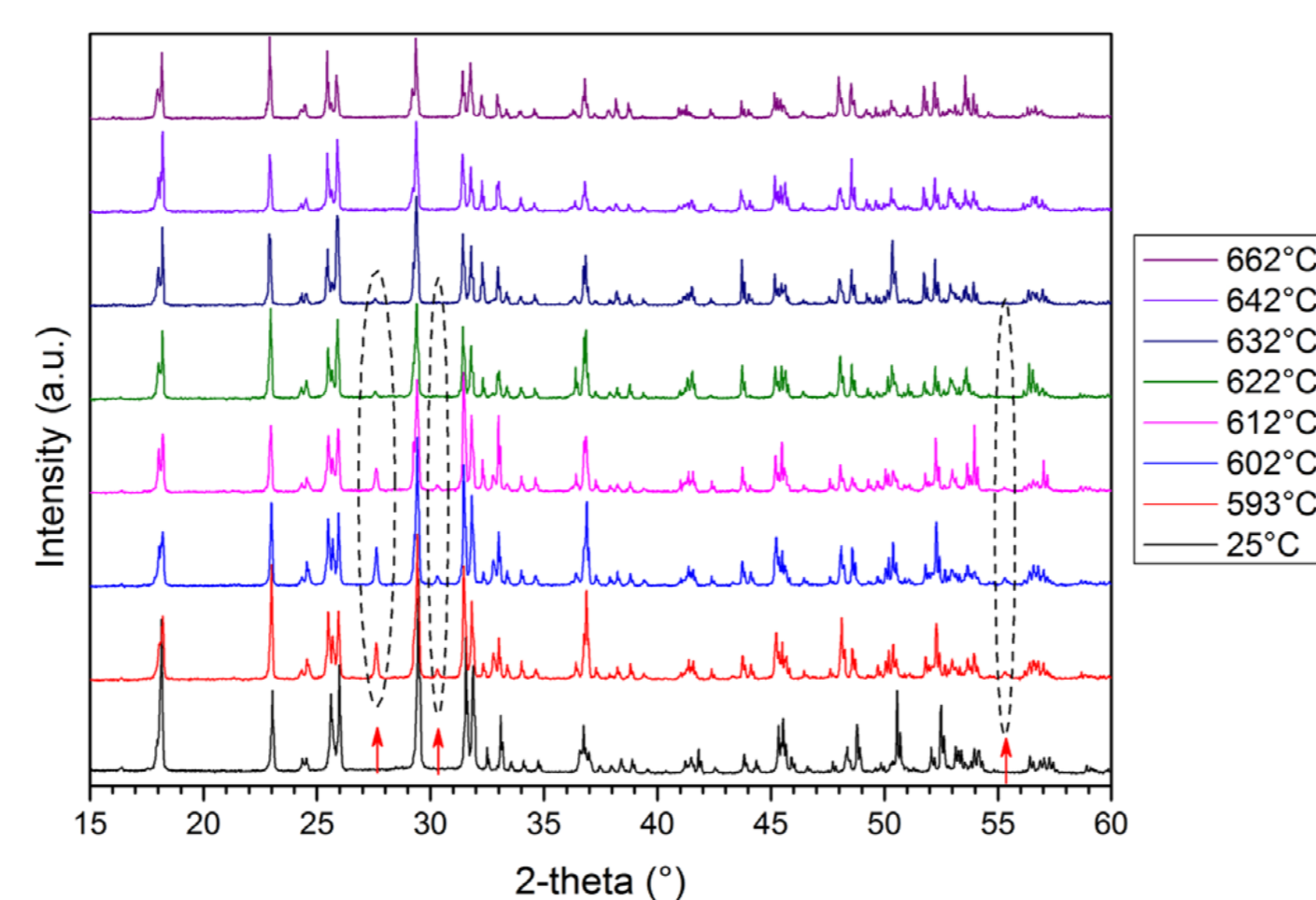


Evaporation of B₂O₃ (13.5%)

DTA traces of BZBO crushed fibers



DRX of BZBO crushed fibers

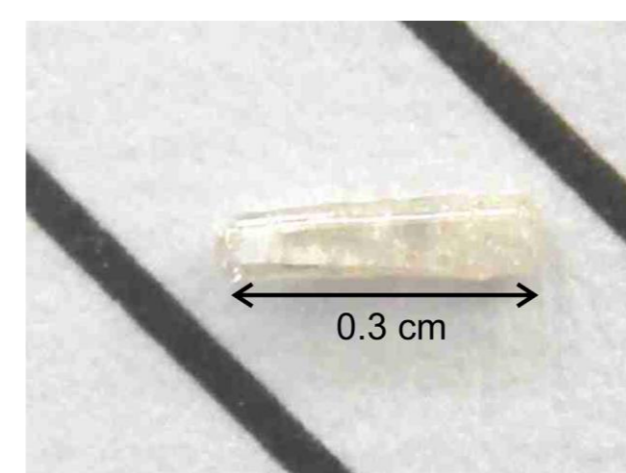


Incongruent behavior of the melt (peritectic type?)

Shift of the melt and crystal composition in the Bi₂O₃-B₂O₃-ZnO

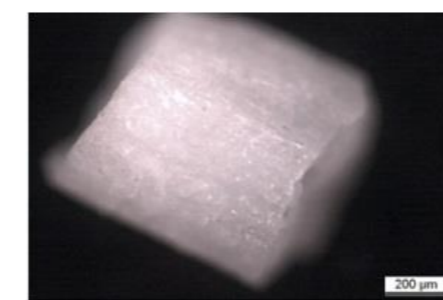
Growth with low pulling rate : 0,15 mm.h⁻¹

Colorless crystal



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LaBGeO₅ : LBGO



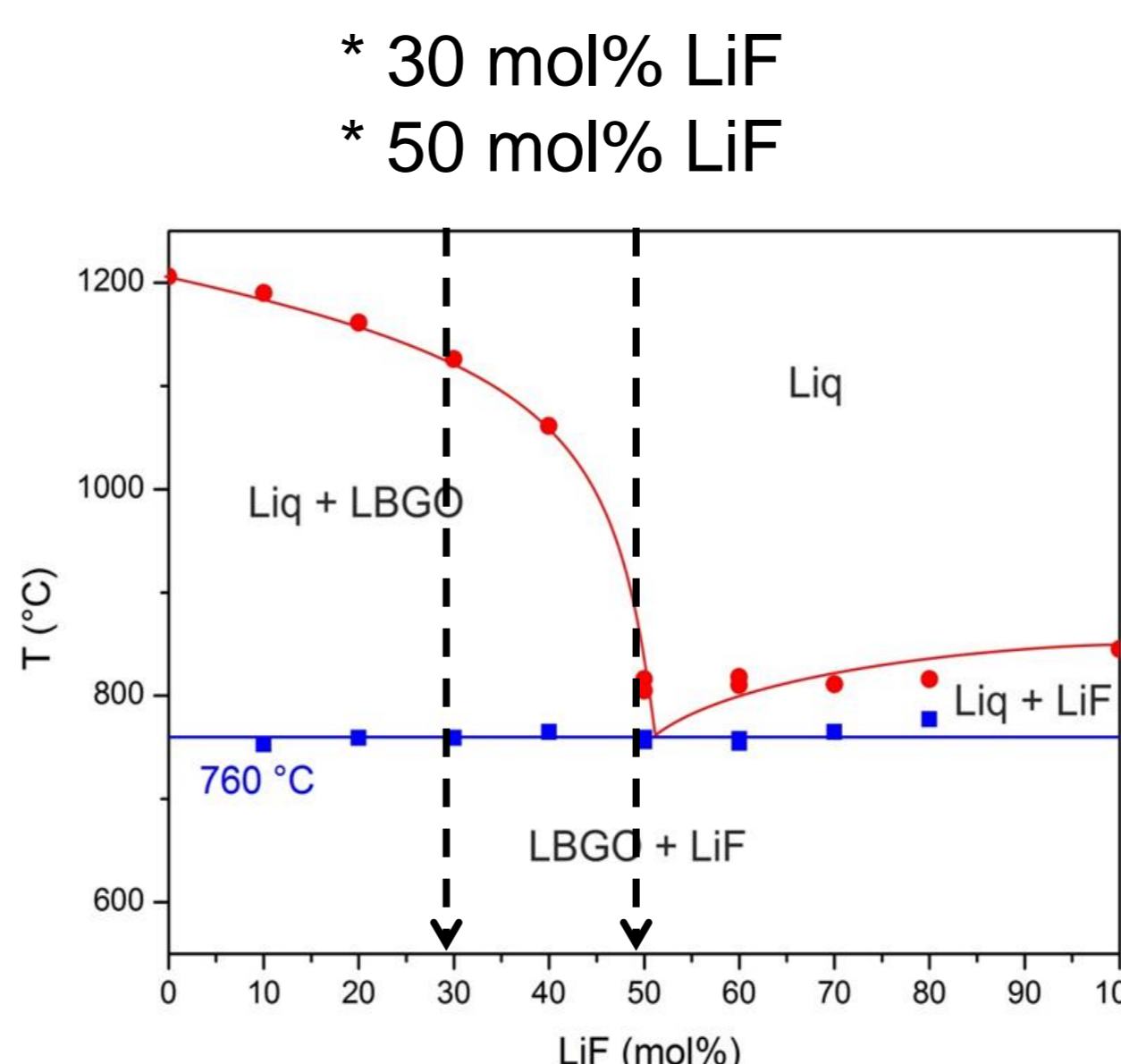
Too high viscosity

Flux growth required

Several fluxes tested :

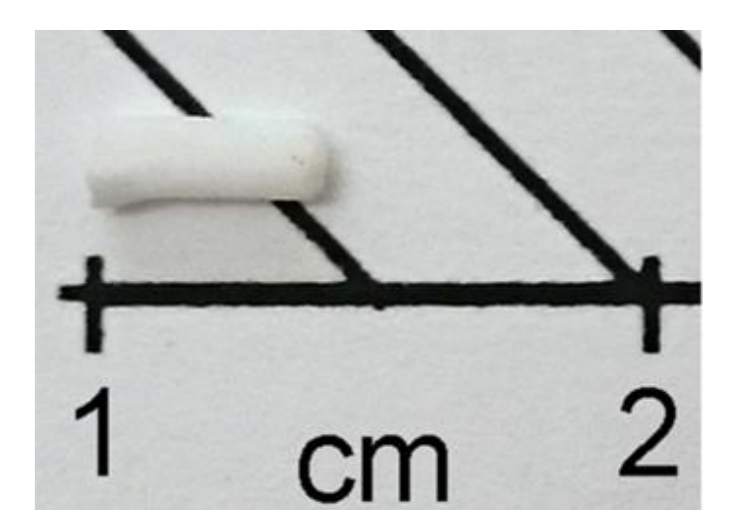
- LiF
- LiF+B₂O₃
- CaF₂
- NaF·B₂O₃
- LiBO₂
- La₂O₃

LiF flux



Failure of growth attempts due to :

- still too high viscosity
- strong LiF evaporation



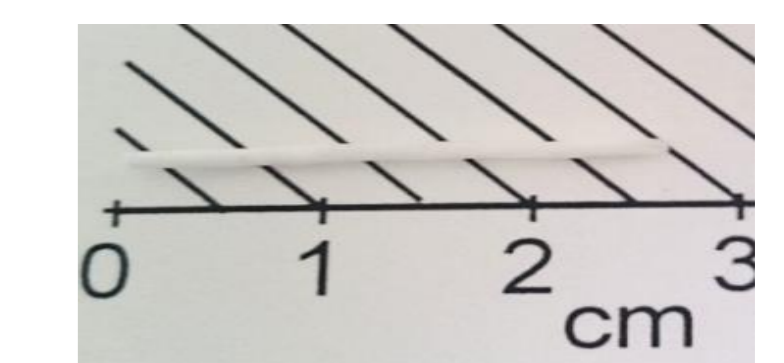
LBGO polycrystalline fiber confirmed by Raman spectroscopy

LiF+B₂O₃ flux

Addition of B₂O₃ in order to decrease LiF evaporation

Flux composition (mol %)	Result of growth trial	Remarks
LBGO 60%-LiF 30%-B ₂ O ₃ 10%	failure	melt too viscous
LBGO 50%-LiF 40%-B ₂ O ₃ 10%	failure	melt too viscous
LBGO 40%-LiF 50%-B ₂ O ₃ 10%	success (1 to 4 cm)	polycrystalline
LBGO 63%-LiF 50%-B ₂ O ₃ 7%	success (1 to 4 cm)	polycrystalline

Example of fibers



Polycrystalline fiber

Raman spectroscopy shows the presence of an unidentified phase

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BaCaBO₃F : BCBF

BCBF fiber and SEM characterization of fibers obtained

V = 12 mm.h⁻¹

Black, opaque fiber



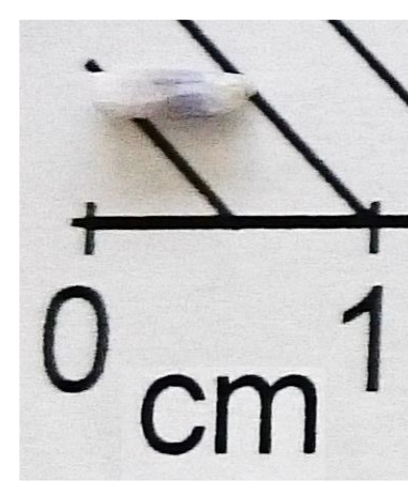
V = 4.2 mm.h⁻¹

Colored, quasi transparent fiber

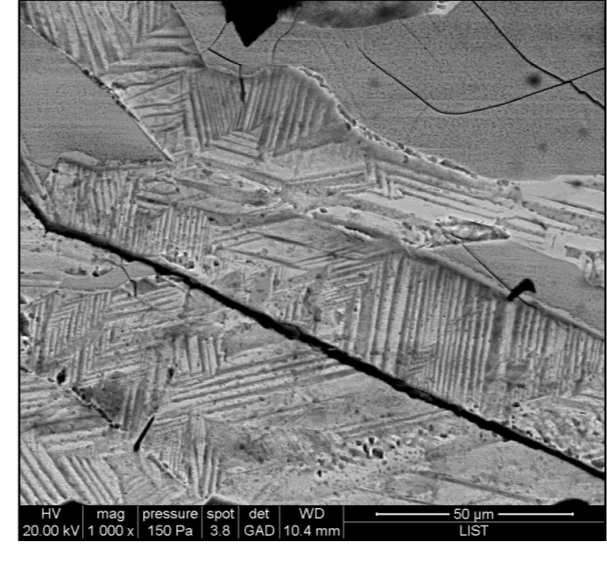
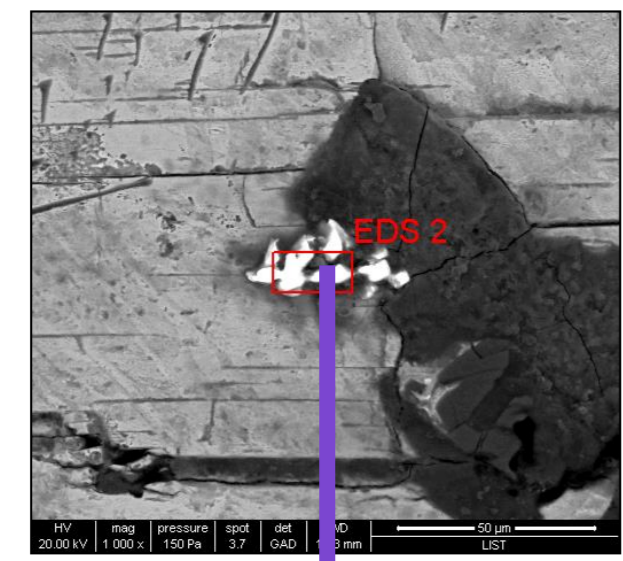
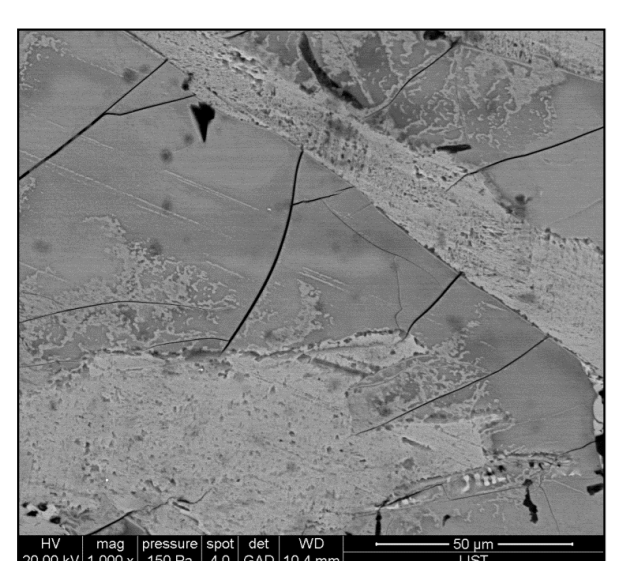


V = 2.4 mm.h⁻¹

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

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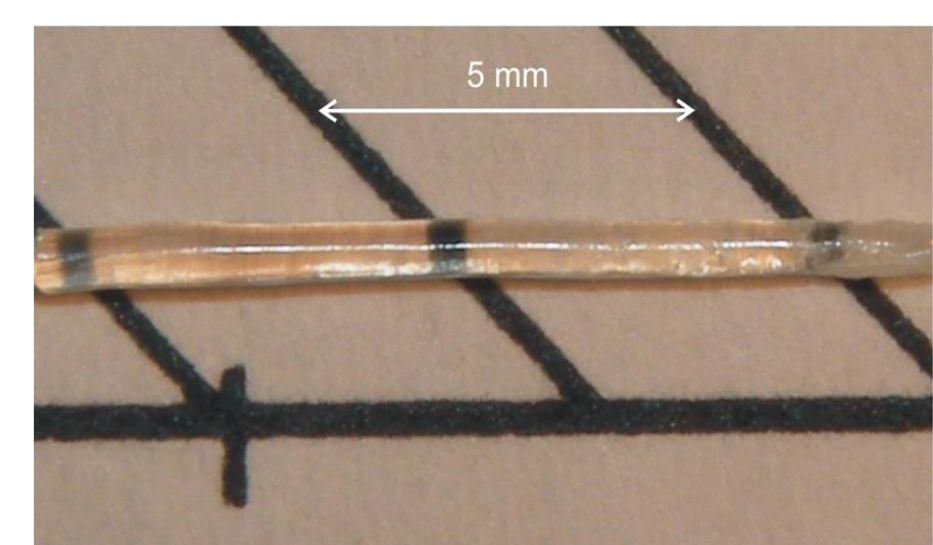
Ca₅(BO₃)₃F : CBF

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 mm



Transparent fiber

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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-B₂O₃ flux needs to be improved and optimized to hope obtaining single-crystal fibers