Winter 1-1-2008

Lecture 9, Part 4: Nucleation, growth and transparent glass-ceramics - Transparent glass ceramics

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Transparent *glass - ceramics*

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www.lamav.ufscar.br

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GUYANA
COLOMBIA
French Guiana (FRANCE)
North Atlantic Ocean
Belém
São Luís
Manaus
Amazon
Fortaleza
Rio Ucayali
Rio Branco
Recife
PERU
Salvador
Cuiabá
BRASÍLIA
BOLIVIA
Corumbá
Belo Horizonte
Vitória
São Paulo
Santos
Rio de Janeiro
South Pacific Ocean
CHILE
PARAGUAY
Paraná
Pôrto Alegre
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ARGENTINA
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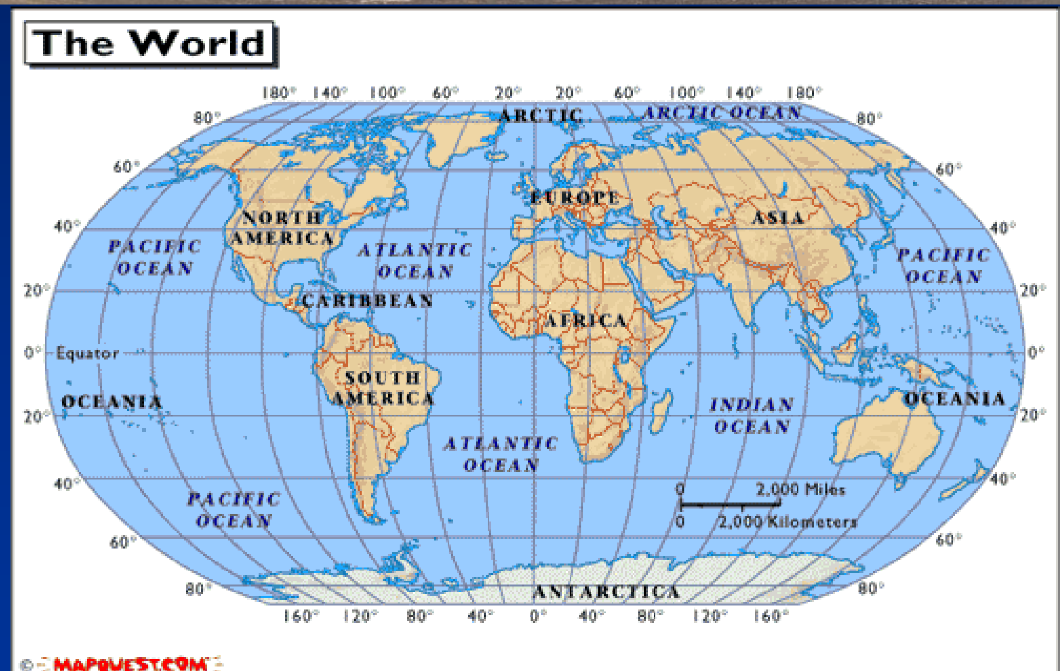
The World
ARCTIC
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Ribeirão Preto
Araraquara
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OUTLINE

- Introduction to glass-ceramics
- Brief literature review on TGC
- Potential applications of TGC
- Conditions for transparency
- Mature TGC – nanocrystals
- New TGC: Properties
  - Sintered aluminate GC — Opt & Mech
  - IR transmitting CG — Opt & Mech
  - Ce: YAG GC for lighting — Opt
  - Laser crystallized GC — Opt
  - PTR GC — Opt & Mech
  - LGHC GC — Opt & Mech
- Surprise....
- Conclusions

Glass-ceramic synthesis

- Entropy vs. T plot
- Heat-treatment plot

INTRODUCTION

null porosity

controlled volume crystallization

GLASS-CERAMICS

designed microstructures: size & shape & uniform grain size, % crystallinity, etc.

high thermal and chemical stability

tougher than glasses

interesting electrical properties

reproducible properties

optical transparency

INTRODUCTION

Applications of transparent glass-ceramics

Thermo-mechanical

- **Cooking ware**
- **Fire resistant plates**
- **Security windows**
- **Telescope mirrors…**

Optical (potential)

saturable absorber media; illumination devices using IR;
heat-resistant materials that absorb UV,
that reflect infrared and are transparent to visible light;
that absorb UV and fluoresce in red/IR;
second harmonics generating;
substrates for LCD devices; optical amplifiers for up-conver;
substrates for arrayed waveguide grating (AWG);
radiation sources of lamps; Laser pumps; Laser media;
Materials for precision photolithography; ring laser gyroscopes; solar collectors; printed optical circuits; etc.

The inventor of GLASS-CERAMICS

S.D. Stookey **discovering GC in the middle 1950s**

LITERATURE REVIEW- PIONEERS OF TGC

STOOKEY,S.D.
***V Int. Congress on Glass*, pp. V/1-8 1959**

BORRELLI, N.F. ELECTRO-OPTIC EFFECT IN TRANSPARENT NIOBATE GLASS-CERAMIC SYSTEMS
***Journal of Applied Physics*, 38 (11): 4243 1967**

BEALL, G.H.; DUKE, D.A.
TRANSPARENT GLASS-CERAMICS
***Journal of Materials Science*, 4 (4): 340 1969**

Recent articles in the next slide

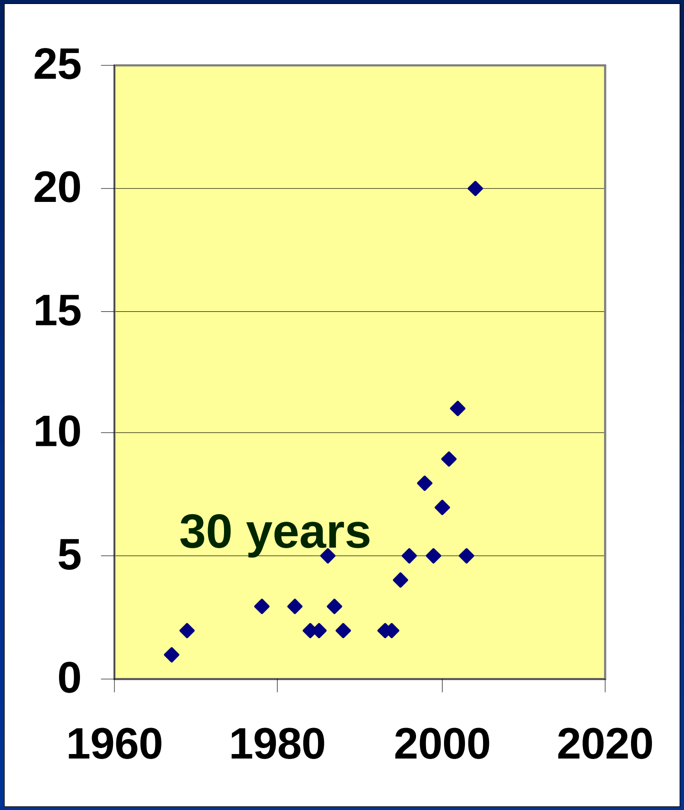
LITERATURE REVIEW (TGC title)

YEAR	112 ISI papers
1967	1
1969	2
1978	3
1982	3
1984	2
1985	2
1986	5
1987	3
1988	2
1993	2
1994	2
1995	4
1996	5
1998	8
1999	5
2000	7
2001	9
2002	11
2003	5
2004	20
2005	5
2006	5

Derwent II

~90 patents

Corning
Schott
Nippon
Others



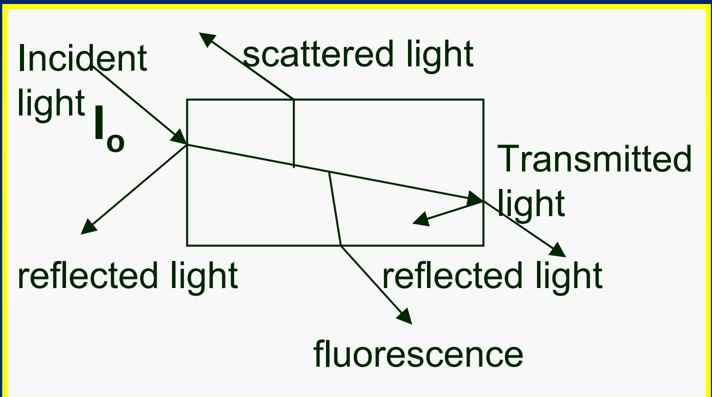
Crystalline phases in TGC

- Β–quartz ss
- Β-eucriptite
- Mullite
- Spinel
- Willemite
- Ghanite
- Forsterite
- β-BBO
- $LiNbO_3$
- $NaNbO_3$
- PbF_2
- LaF_3
- ZnO
- Etc.

Most TGC have nanosize crystals & small crystallized volume fraction (~ 50% or less)

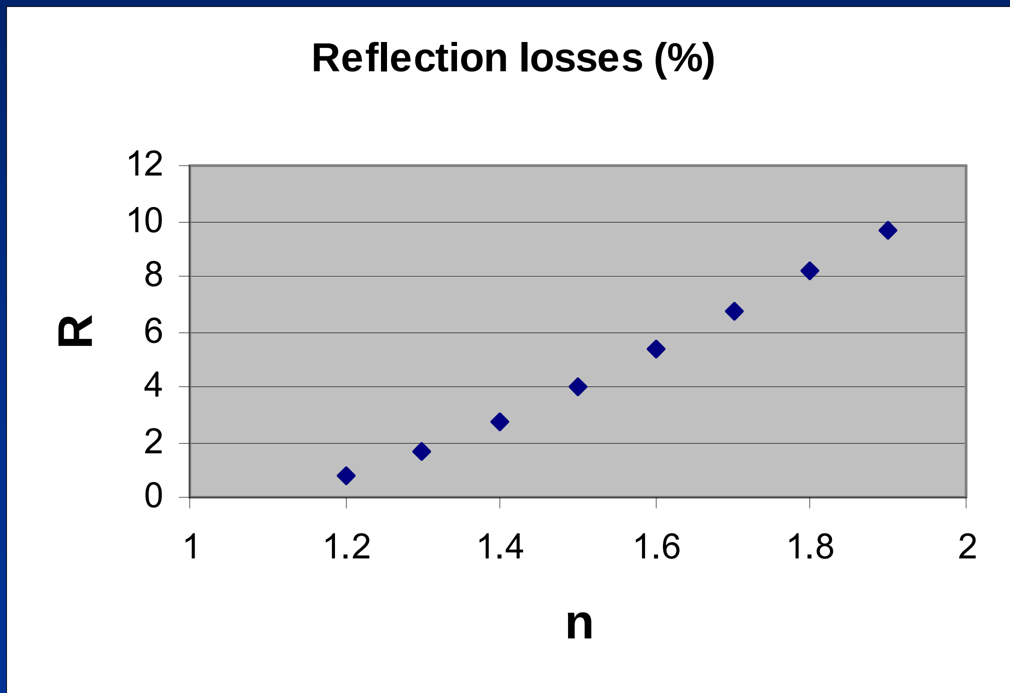
THEORY

Light attenuation { **atomic absorption (β)** / **scattering (S)** } + **surface reflection (R)**



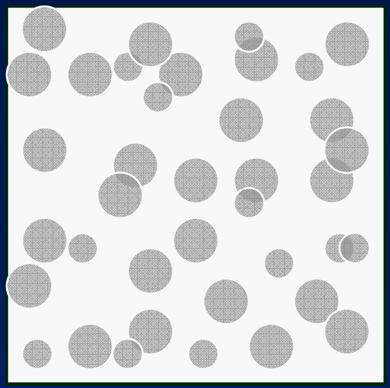
$$I = I_o(1-R)^2 \exp(-(\beta + S)x)$$

$$R = \left(\frac{n-1}{n+1}\right)^2$$



Conditions for transparency

Transparent glass-ceramics



crystal size << wavelength of light

Basic requirements ⇒ low birefringence

$n_{glass} \cong n_{crystal}$

Examples of commercially mature TGC

Corning's VISION

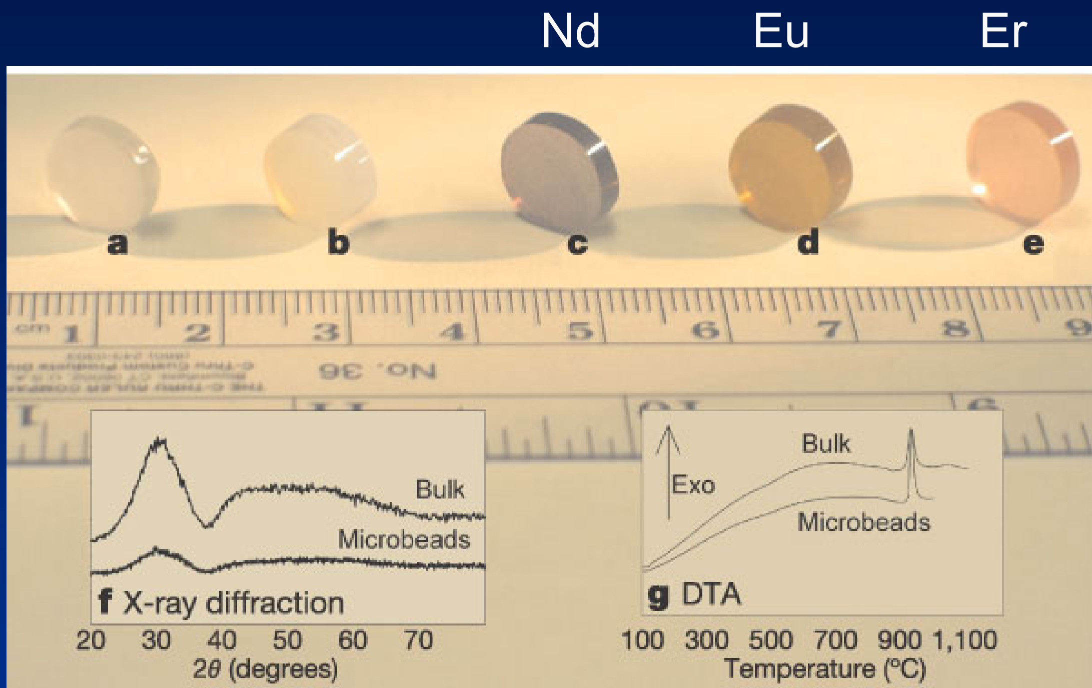
VLT 8.2 m Zerodur mirror on its way to Paranal Observatory, Chile, Dec. 97/ Schott

ROBAX – Schott
NEOCERAM – NIPPON
KERAGLASS- Corning/ St. Gobain

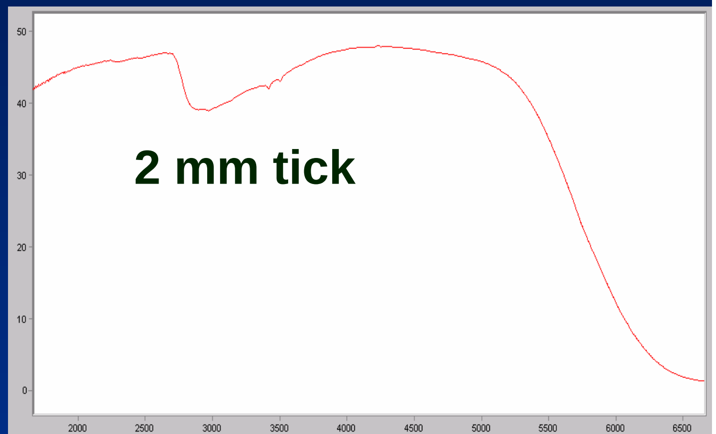
CERAN- Schott

NEW
TRANSPARENT GC
(yet on the development stage)

Bulk glasses and ultrahard nanoceramics based on alumina and rare-earth oxides by A. Rosenflanz et al. ***Nature* 430**, 761 - 764 (August 2004).



IR transparent

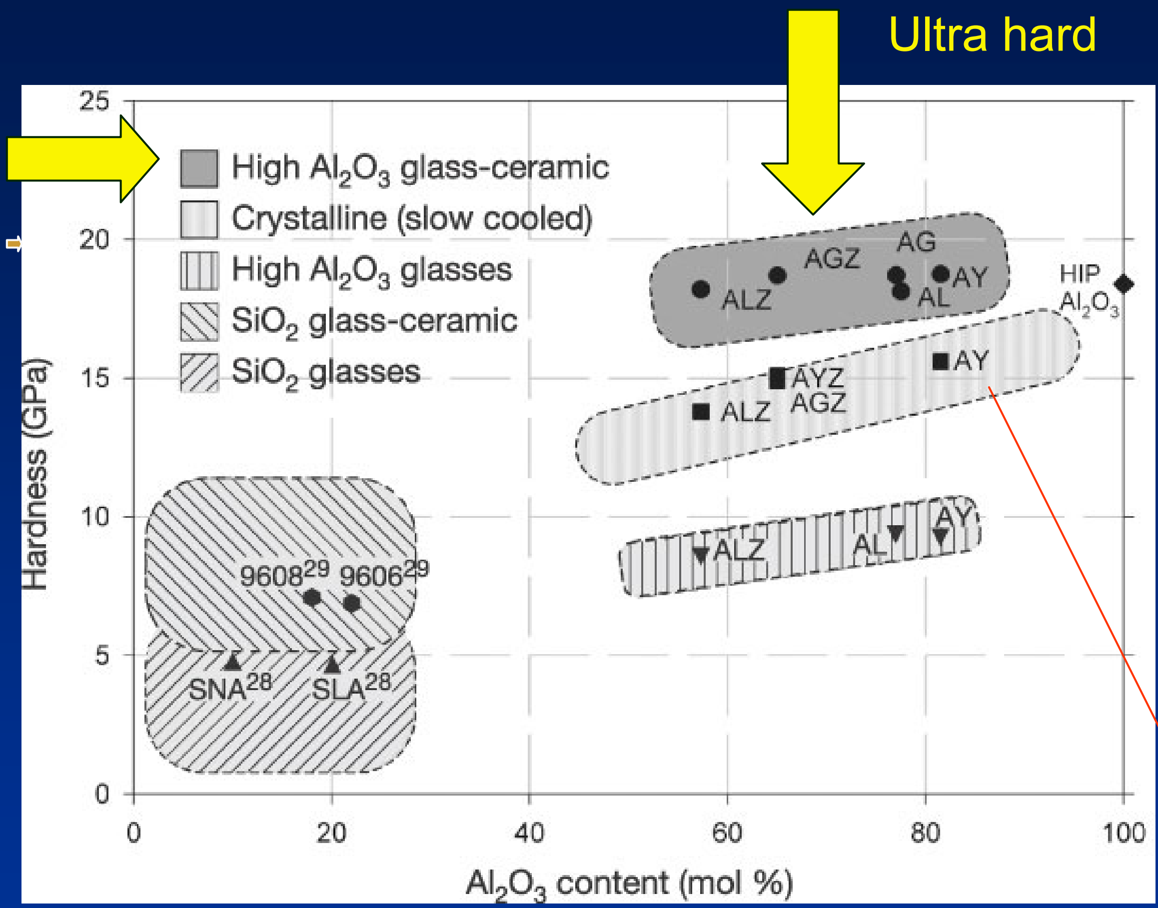


50-90% Al_2O_3

a, **b**: no dopants; **c** 5wt% Nd_2O_3; **d** 5wt% Eu_2O_3; **e** 5wt% Er_2O_3.
All except **b** were hot-pressed at 905 °C at 34 MPa for 360 s.

Material **b** was hot-pressed for 1,200 s inducing partial crystallization, giving the opalescent appearance.

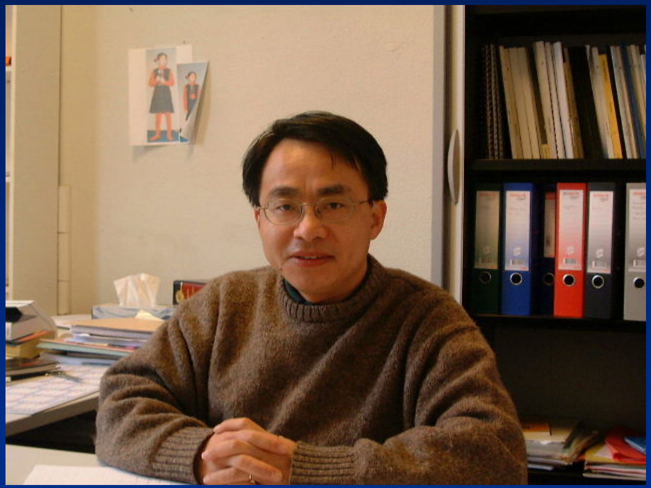
High alumina glasses and GC



Hardness against Al2O3 content. High-alumina glasses and glass-ceramics surpass other oxides : BeO, MgO, Y2O3, ZrO2, TiO2, Y3Al5O12, Corning 9606 and 9608 GC, and are comparable to pure ***a*****-Al2O3 and** ***b*****-Si3N4.**

These compositions were crystallized directly from the melt during slow cooling.

IR transmitting chalco-sulfide glass-ceramics

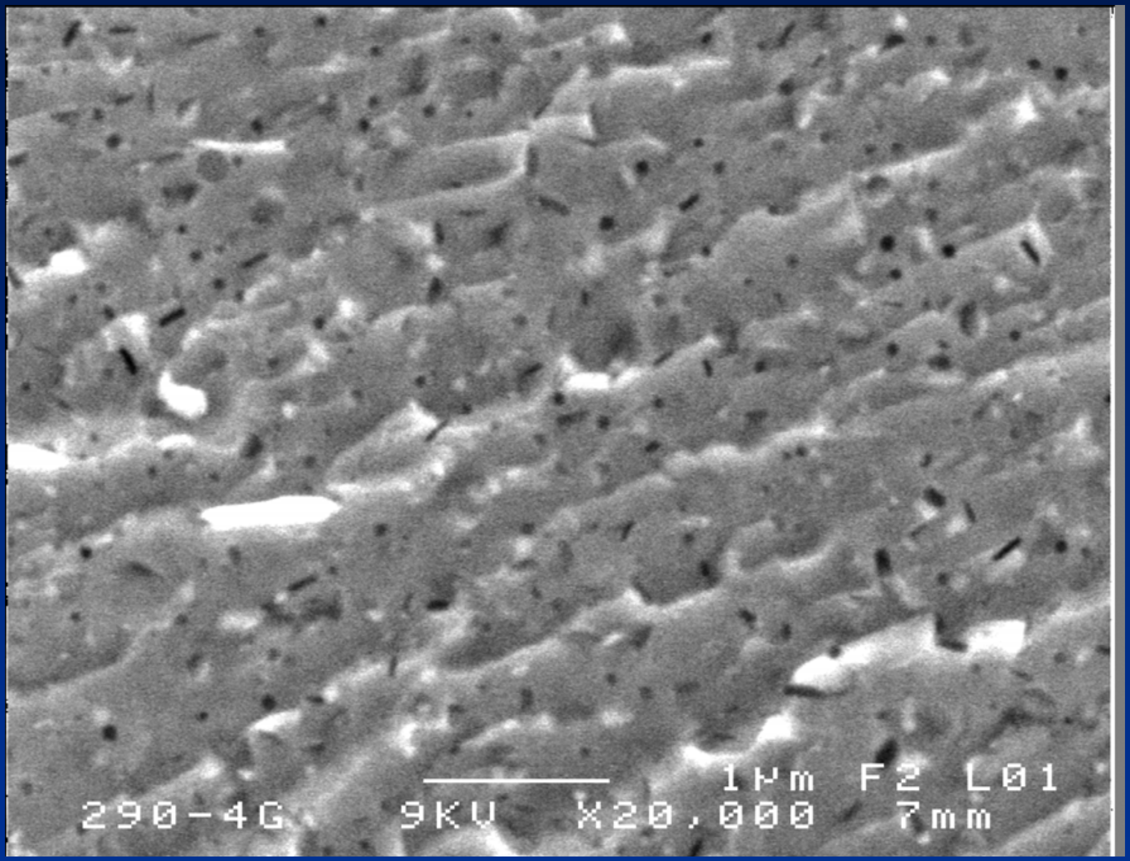


Ge-Sb-S-Cs-Cl glass with CsCl crystals

X. Zhang et. al. , J. Non-crystalline Solids 337 (2004) 130
Lab. glasses and ceramics, University of Rennes, France

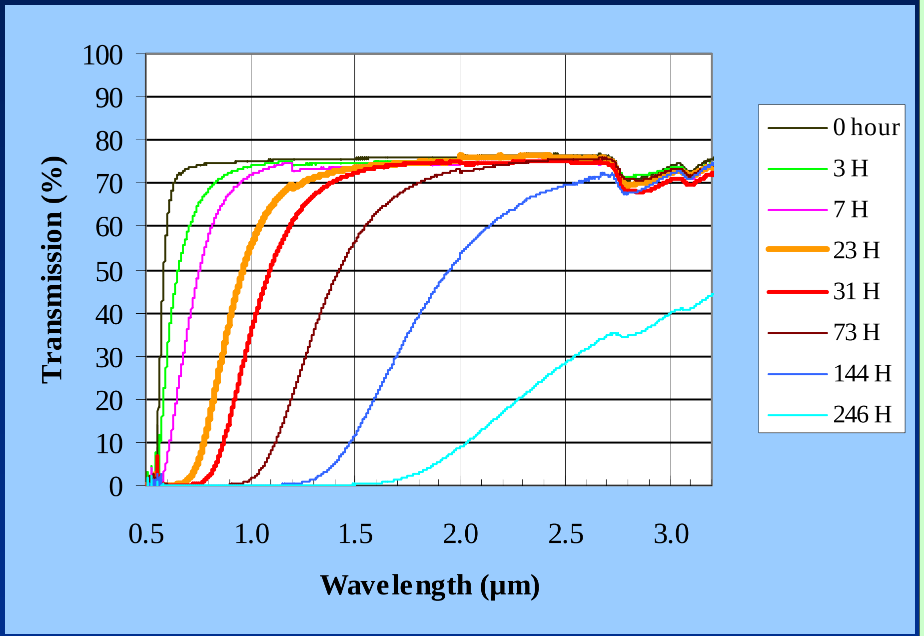
Typical microstructure of IR glass-ceramics

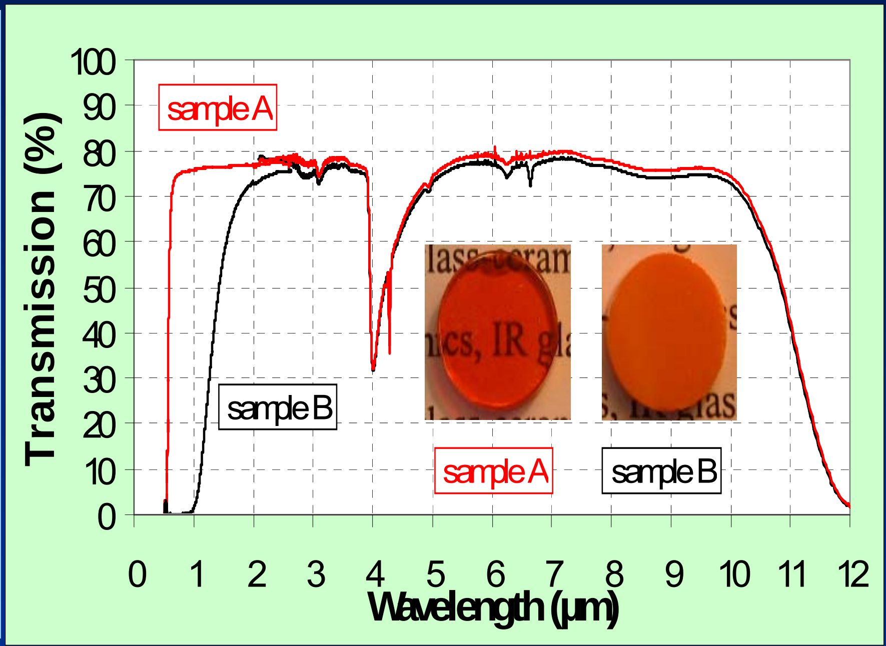
100nm CsCl
crystals



Zhang et. al.

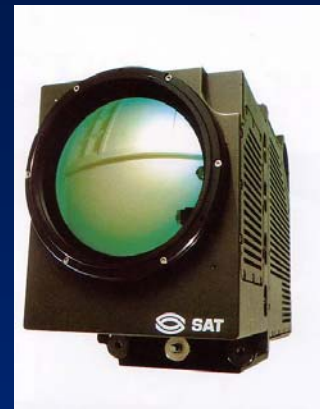
IR transmission *versus* crystallinity



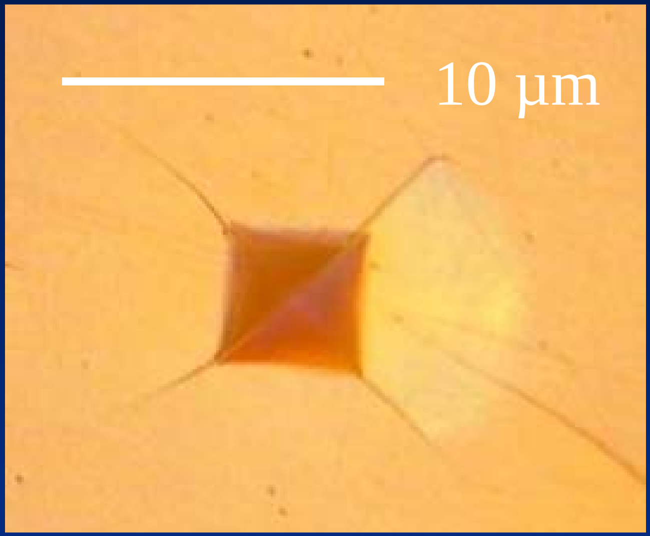


Zhang et. al.

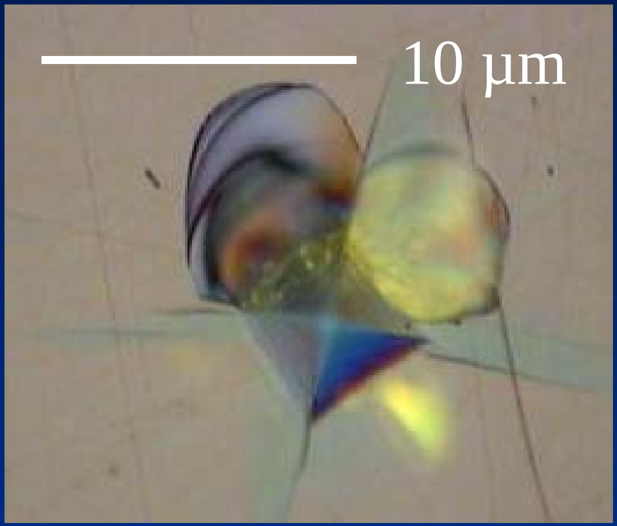
Night vision



Resistance to fracture propagation



GC



Glass

Zhang et. al.

Glass-Ceramic for Solid State Lighting - *White LED*

Ce:YAG-GC

Setsuhisa Tanabe
Kyoto University, Kyoto, Japan

Shunsuke Fujita, Akihiko Sakamoto, Shigeru Yamamoto
Nippon Electric Glass, Otsu, Japan

Presented at the ACerS meeting, Baltimore, April 2005

Solid-State Lighting (future)

Promise of LEDs for illumination

	Efficiency	Life
Incadescent Light Bulb	16 *lm / W*	1000*h*
Fluorescent Lamp	80 *lm / W*	10,000*h*
Today's white LED	60 *lm / W*	20,000*h*
Future white LED	200 *lm / W*	100,000*h*

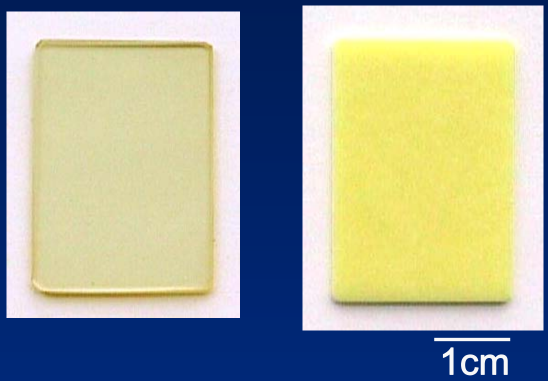
Efficiently bright, broad spectrum, long-lifetime…

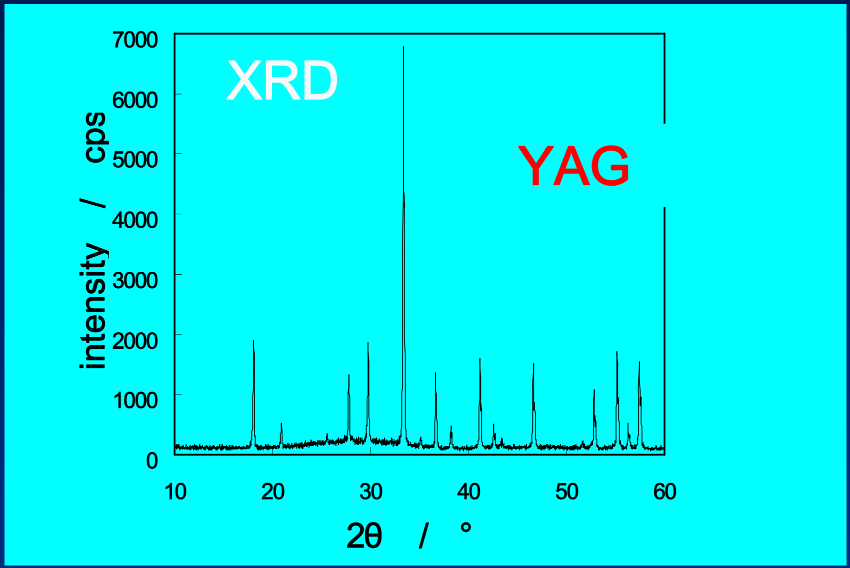
S. Tanabe et al.

YAG-GC from glass- microstructure

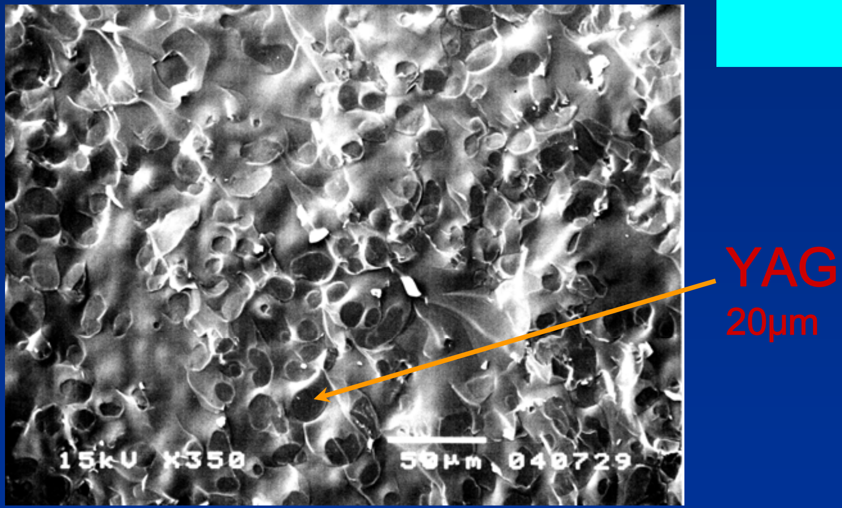
As-made

Cerammed





SEM



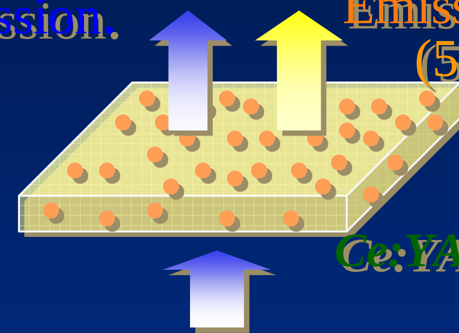
60%
Crystalinity
(wt%)

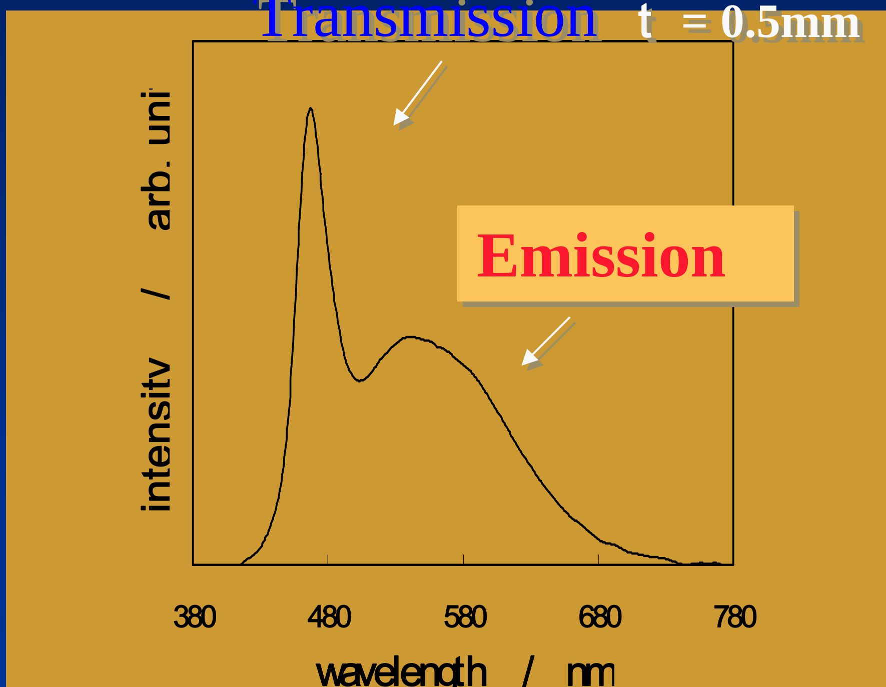
S. Tanabe et al.

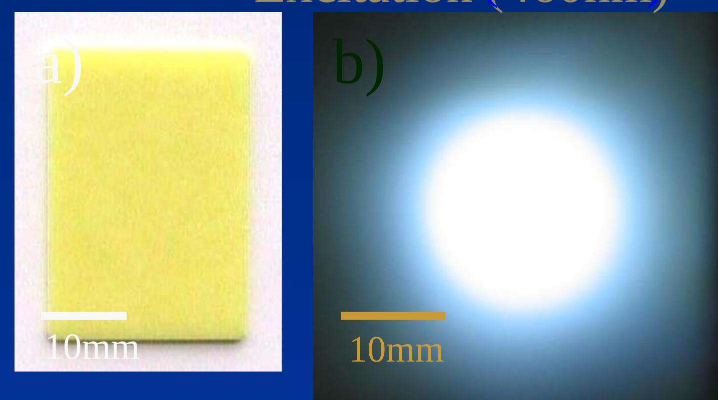
Moderate transmission of blue

Yellow fluorescence

White light







a) Ce:YAG GC

b) White light emission from Ce:YAG G.C.

Laser crystallization in Nagaoka

Takayuki Komatsu & collaborators
(Benino, Ihara, Fujiwara, et al.)

Department of Chemistry
Nagaoka University of Technology
Japan

Example: Appl. Phys. Lett., 82 (2003) 892, 83 (2003) 2796.

Laser crystallization in glass

Nagaoka

Rare-earth (Samarium) atom heat processing

1. CW Nd:YAG laser irradiation to Sm_2O_3 or Dy_2O_3 containing glasses
2. Absorption and non-radiative relaxation

Irradiated region is heated → Crystallization

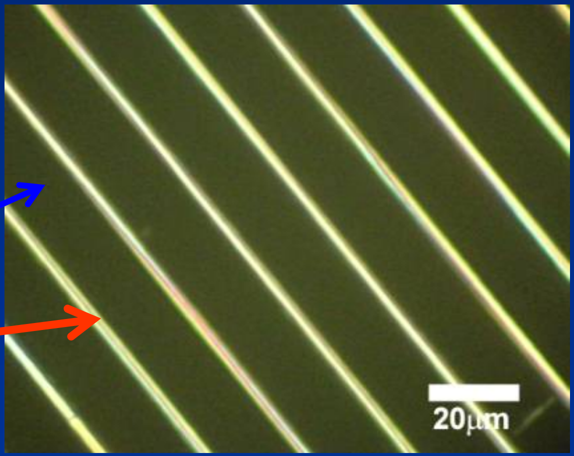
Writing of nonlinear optical/ferroelectric crystal dots and lines

- Sm_2O_3-BaO-B_2O_3 → β-BaB_2O_4
- Sm_2O_3-Bi_2O_3-B_2O_3 → $Sm_xBi_{1-x}BO_3$
- Sm_2O_3-MoO_3-B_2O_3 → β'-$Sm_2(MoO_4)_3$
- Sm_2O_3-K_2O-P_2O_5 → $KSm(PO_3)_4$

Sm_2O_3-Bi_2O_3-B_2O_3 glass

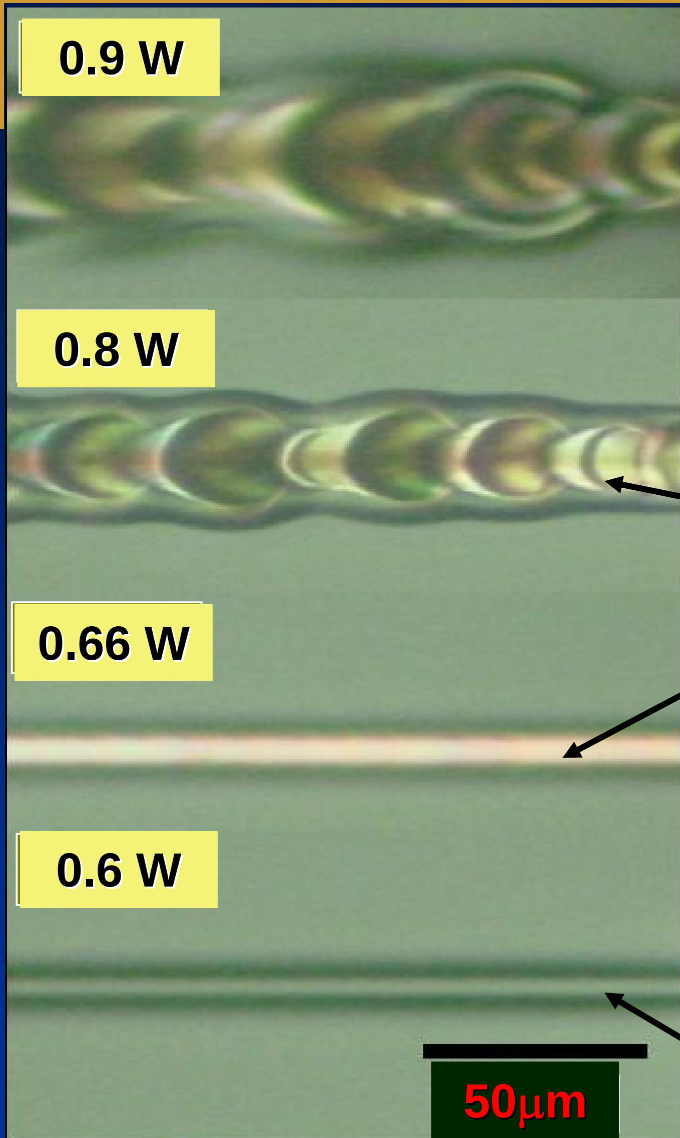
$Sm_xBi_{1-x}BO_3$ crystal

Power: 0.66W
Scanning speed: 10μm/s



20,000 J/cm^2

Polarization optical microscope



長岡技術科学大学

$10Sm_2O_3.35Bi_2O_3.55B_2O_3$ glass

Komatsu

$T_g=474^oC$, $T_x=574^oC$

$Sm_xBi_{1-x}BO_3$

crystal

Temp. >> T_x

Temp. < T_x

Refractive index change

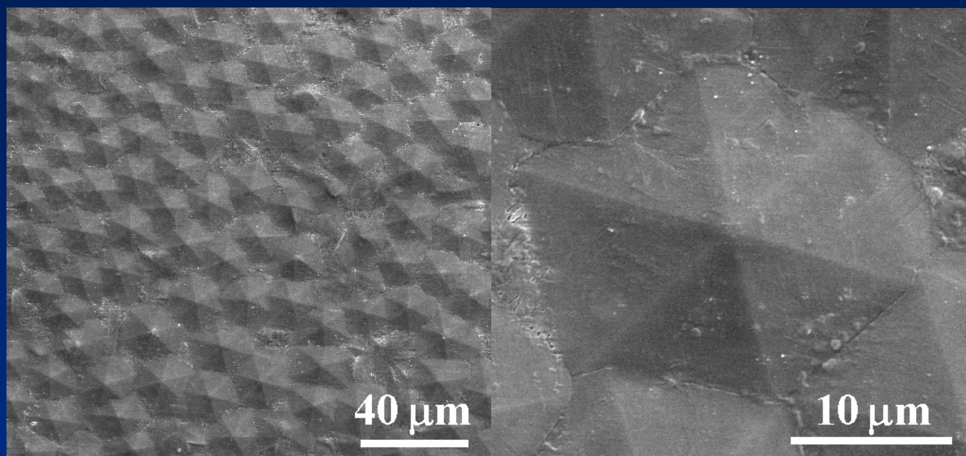
Laser crystallization in São Carlos

C. A. C. Feitosa, L. J. Q. Maia, A. L. Martinez, A. C. Hernandes, Valmor R. Mastelaro,

IFQSC, University of São Paulo, São Carlos, Brazil

$40BaO - 45B_2O_3 - 15\ TiO_2$ (BBT)

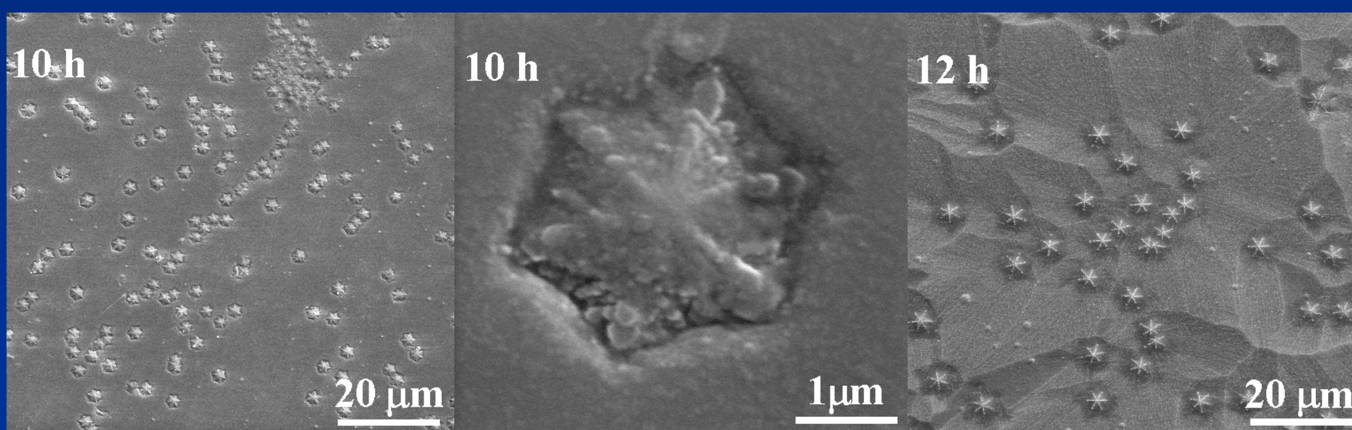
Microstructures from two crystallization processes



BBT glass after irradiation with CO_2 laser (λ= 10.6 µm) 4 min, 40 W/cm^{2}.

= 10,000 J/cm^2

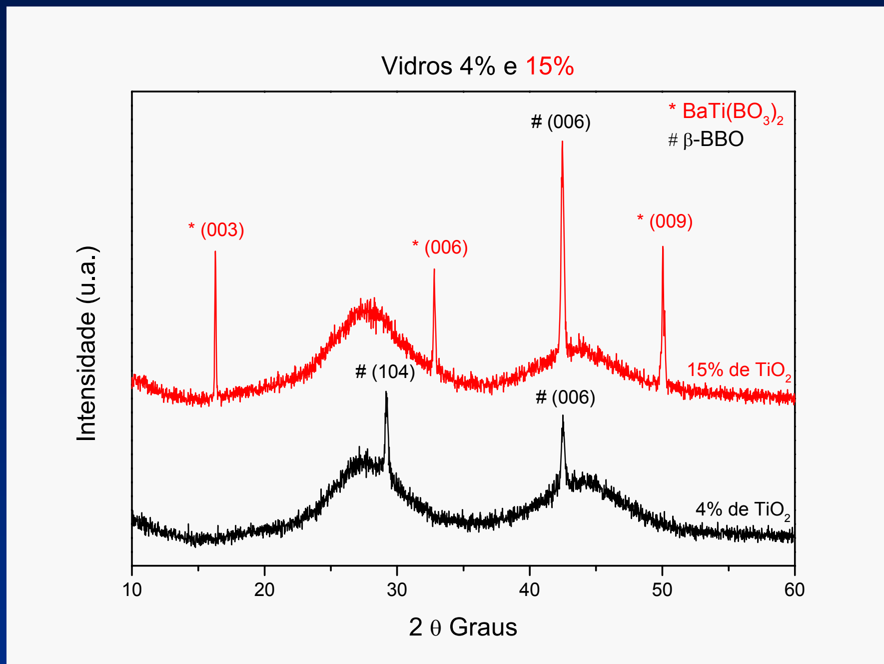
Glass at 300°C (T_g = 580 °C)

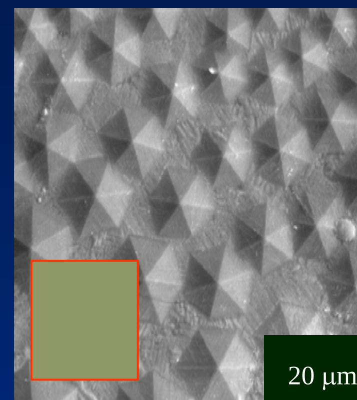


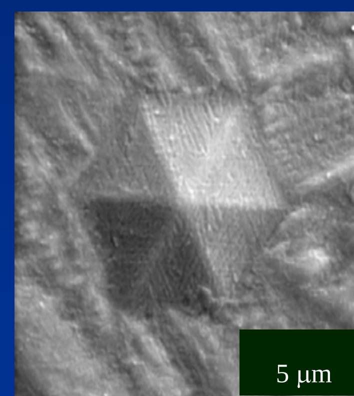
BBT GC in resistive furnace at 620°C.

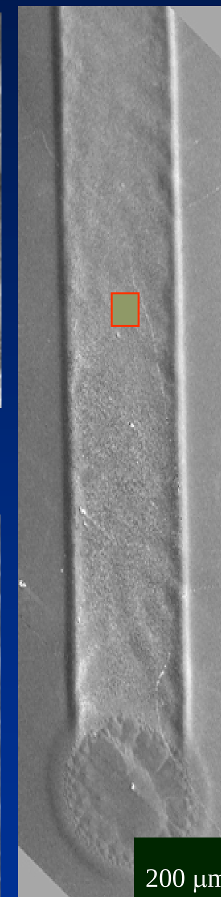
Mastelaro et. al.

Surface crystallization of BBT glass







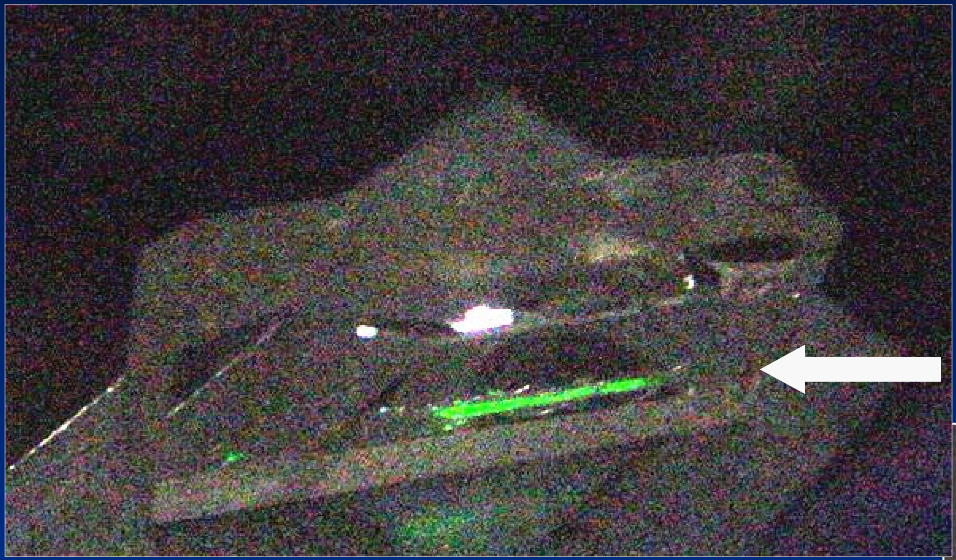


It is possible to produce policrystalline lines.

Details; crystals within the line and diffraction pattern

SHG in partially crystallized BBT glass

Mastelaro et. al.



Laser beam
Nd:YAG (λ = 1064 nm)

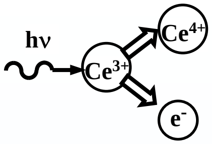
Second harmonic generation

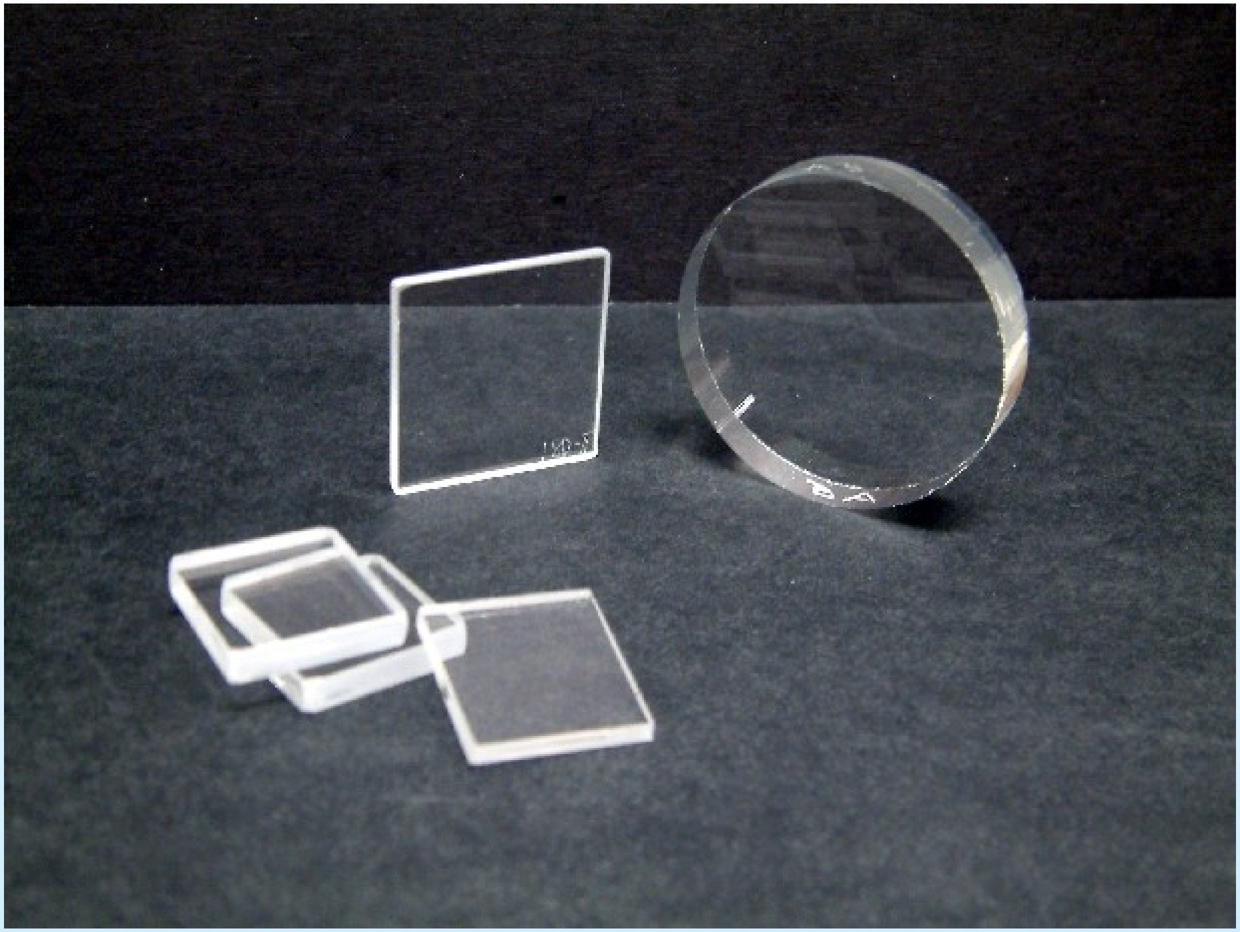
PTR Glasses
Oxy fluor bromide glasses

S.D. Stookey et al. (1954) – Corning, USA
L.B. Glebov et al. (1990) - Vavilov SOI, Russia + Creol/ UCF, USA

- Composition
- **Major: SiO_2, Na_2O, ZnO, Al_2O_3**
- **Minor: K_2O, F, Br**
- **Dopants (~200 ppm): Ag, Ce, Sb, Sn**
- **Impurities (< 2 ppm): transition metals**

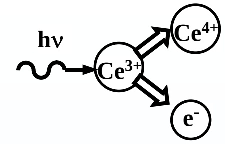
PTR glass is a F-Br sodium-zinc-aluminum-silicate glass doped with Ag, Ce, Sn and Sb

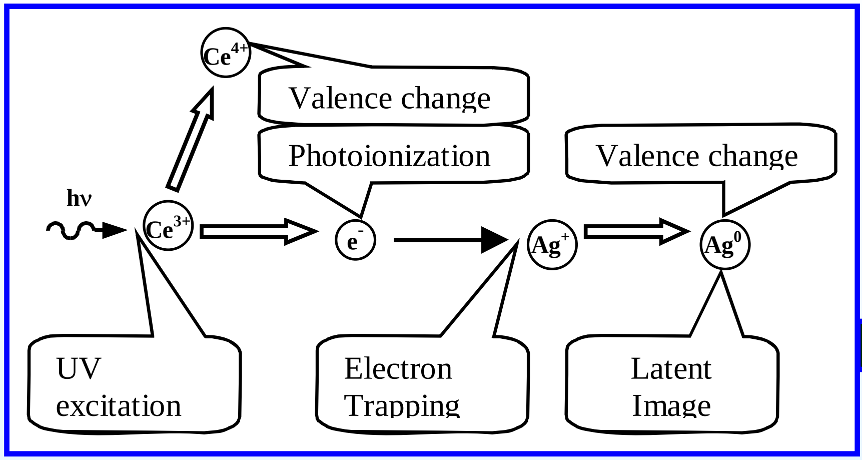


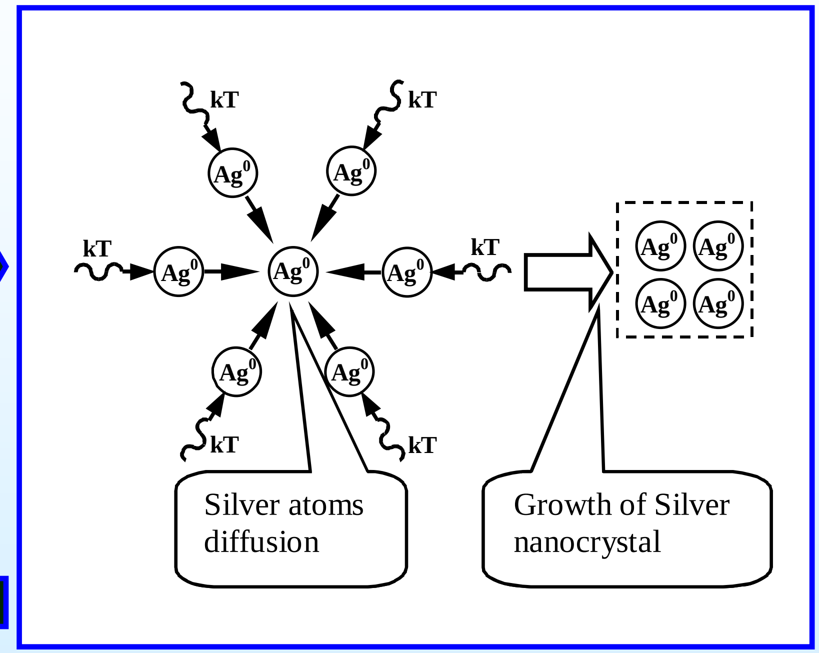


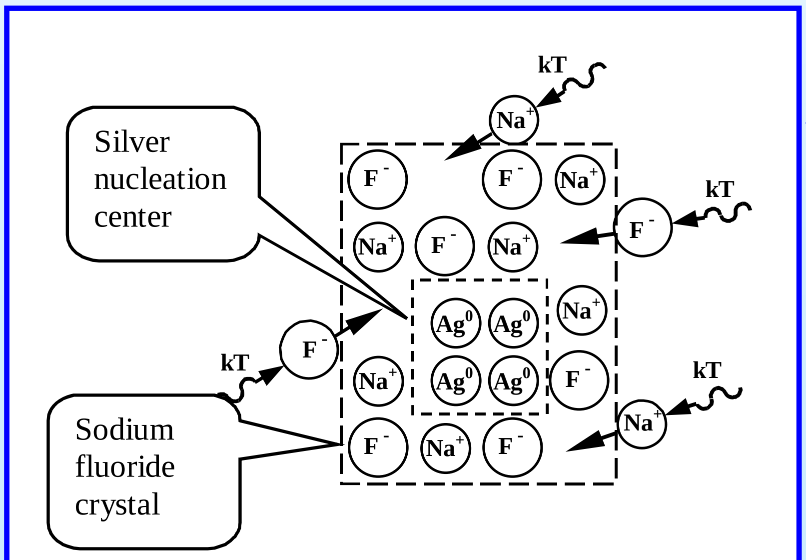
Current technology at UCF/CREOL - optical quality PTR glasses with aperture up to 50 mm.

Mechanism of photo-thermo-crystallization



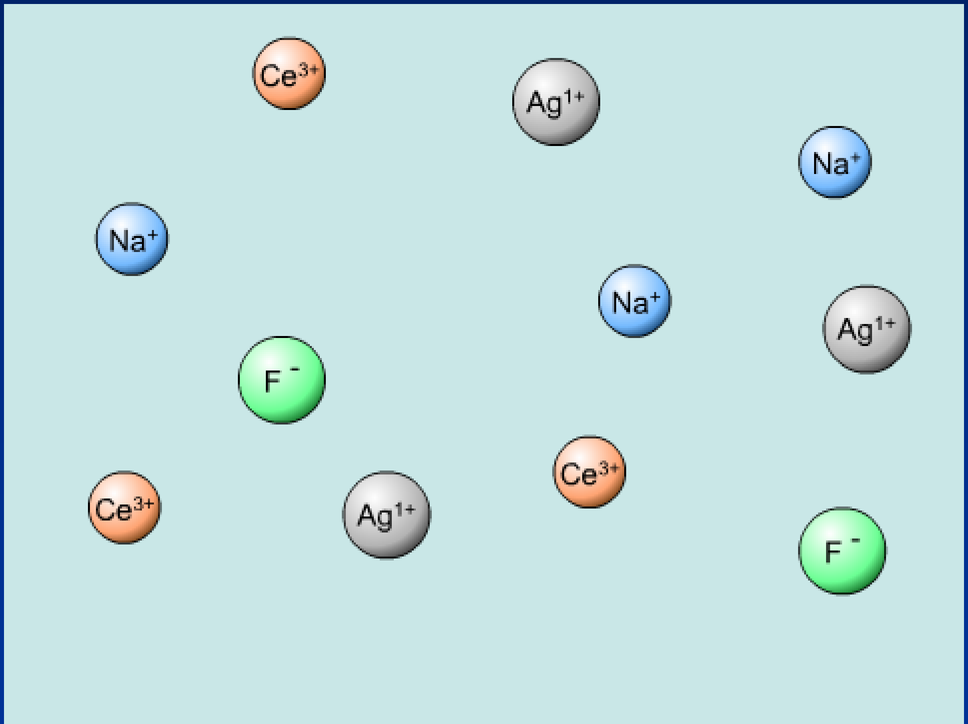


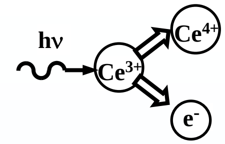




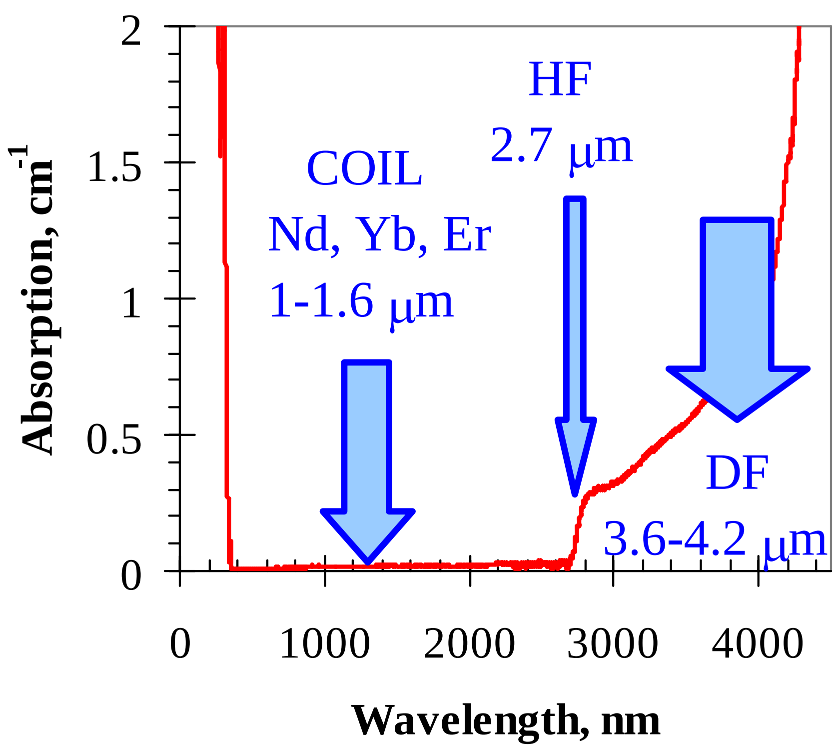
3D image (hologram) of object is transformed to the phase pattern (refractive index variations) caused by selective NaF crystal distribution in accordance with the UV intensity distribution in glass interior.

PTRG (only the active ions are shown) Proposed mechanism of photo induced crystallization





Absorption spectrum of photo-thermo-refractive glass

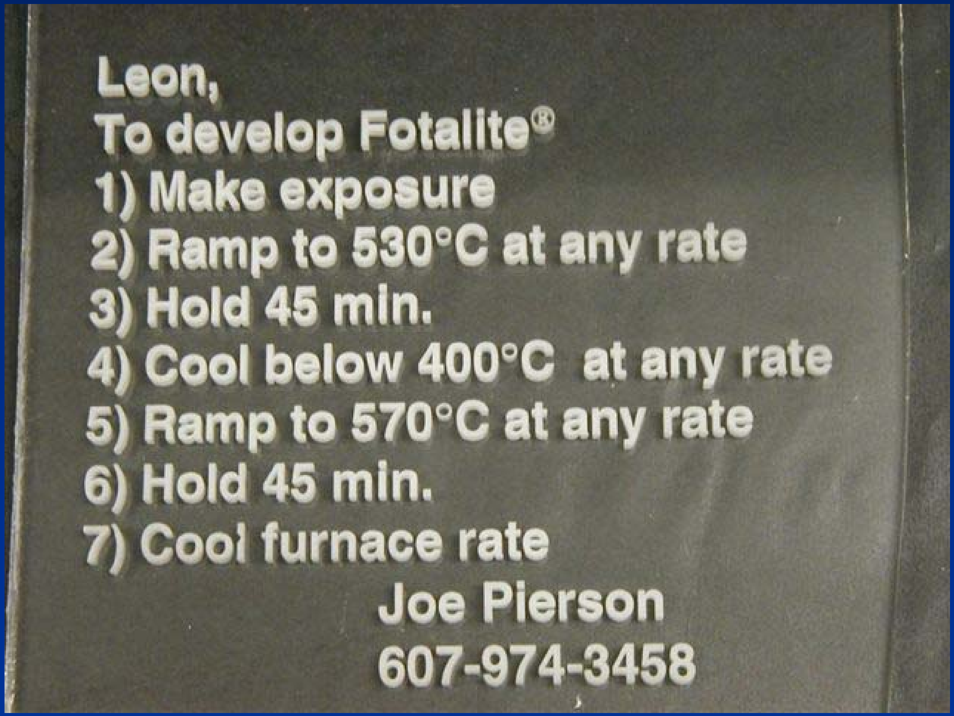


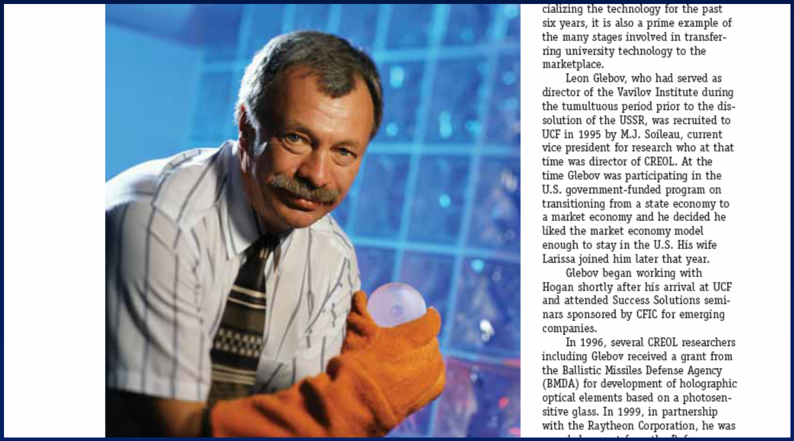
No detectable absorption in the range of 1 μm
Absorption of hydroxyl in the range of 4 μm

PTR glasses

S.D. Stookey et. al.

Corning's Fotalite





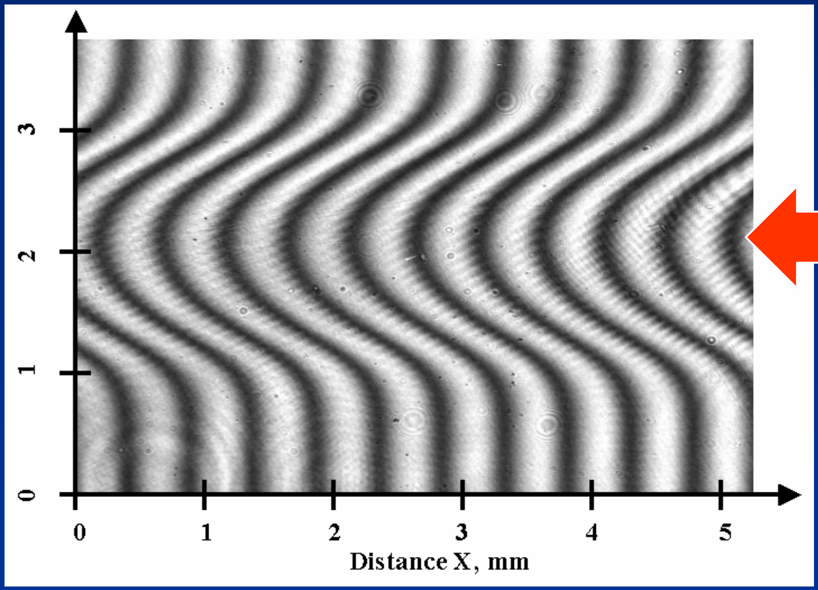
cializing the technology for the past six years, it is also a prime example of the many stages involved in transferring university technology to the marketplace.

Leon Glebov, who had served as director of the Vavilov Institute during the tumultuous period prior to the dissolution of the USSR, was recruited to UCF in 1995 by M.J. Soileau, current vice president for research who at that time was director of CREOL. At the time Glebov was participating in the U.S. government-funded program on transitioning from a state economy to a market economy and he decided he liked the market economy model enough to stay in the U.S. His wife Larissa joined him later that year.

Glebov began working with Hogan shortly after his arrival at UCF and attended Success Solutions seminars sponsored by CFIC for emerging companies.

In 1996, several CREOL researchers including Glebov received a grant from the Ballistic Missiles Defense Agency (BMDA) for development of holographic optical elements based on a photosensitive glass. In 1999, in partnership with the Raytheon Corporation, he was

Creol's PTRG Hologram **Leon Glebov et. al.**

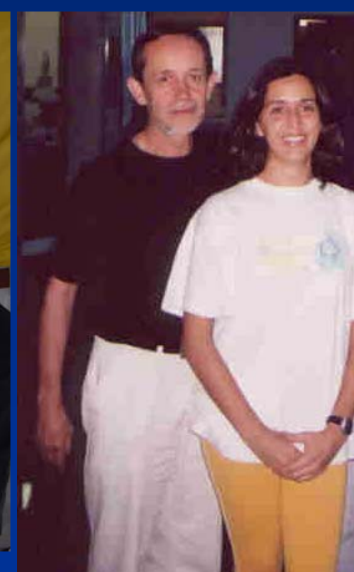


LARGE GRAIN, HIGHLY CRYSTALLINE, HIGHLY TRANSPARENT GC

T. Berthier, V.M. Fokin, E.D. Zanotto
LaMav- Federal University São Carlos, Brazil

Vlad Fokin

Thiana Berthier



STRATEGY

Simultaneous compositional variation

of solid solution crystals and glassy matrix

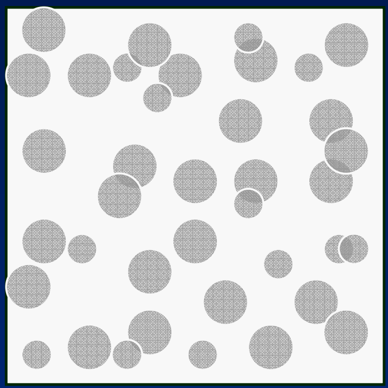
decreases Δn

New type of transparent glass-ceramic

small or large grain size

high crystallized volume fraction

OPTICAL PROPERTIES



Transmission Spectra

200 nm – 1100 nm

- Crystal morphology
- Grain size
- Degree of crystallinity OM

Transmittance measured for different sample thicknesses

Estimated parameters (P_1 and P_2):

$$\frac{I}{I_0} = P_1 \exp(-P_2 x)$$

$P_1 = (1-R)^2$

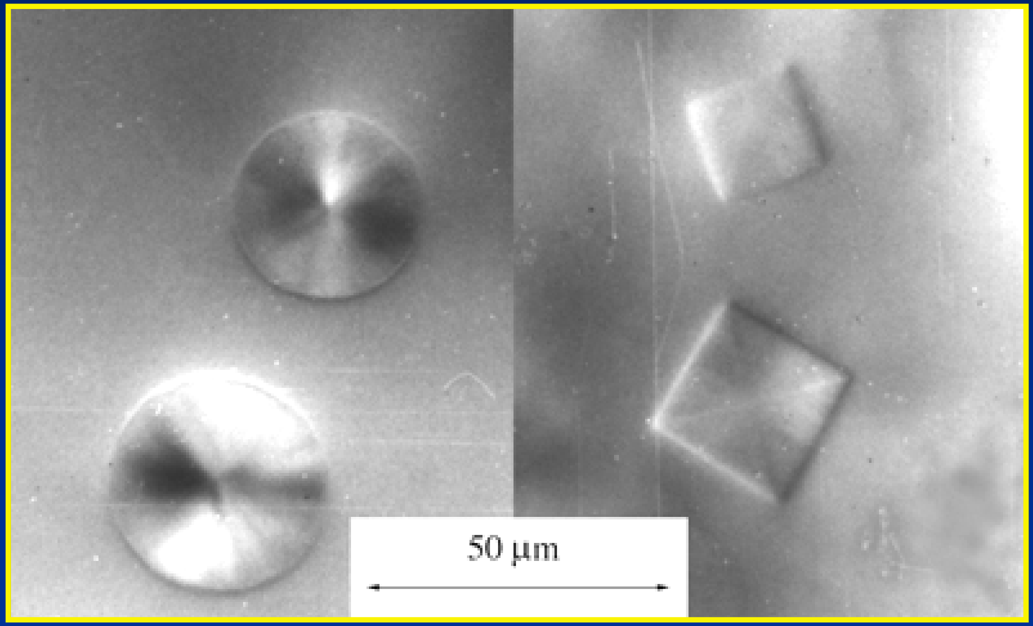
$P_2 = (\beta+S)$

MICROSTRUCTURES

The crystals are solid solutions: $TA_{4+2x}AE_{4-x}[GF_6O_{18}]$ $(0 \le x \le 1)$

Their morphology can vary from

J, spherical to V8, cubic



T = trace element

A = alkali

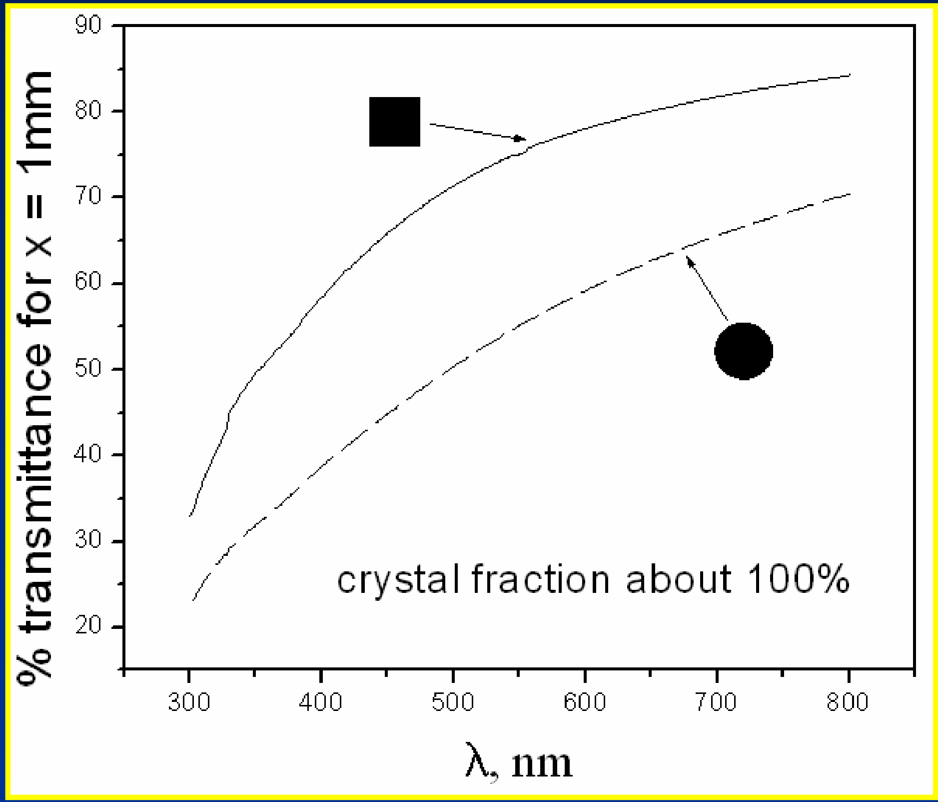
AE = alkaline earth

GF = Si, P, B

TRANSMITTANCE

Morphology

Distinct crystal shapes ⟶ Different transmittances



V8, cubic 5-6 μm
J, spherical 7-8 μm

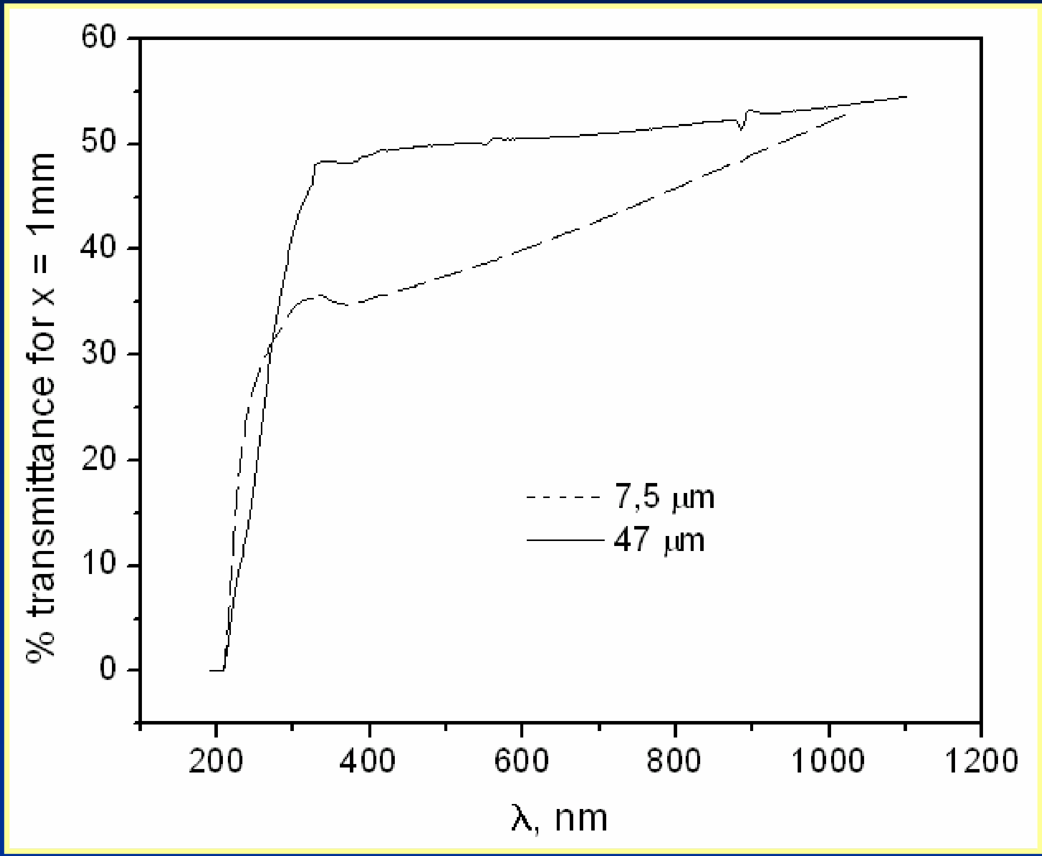
crystal/crystal Interfaces are quite different for spherical and cubic crystals

Best transmittance ⟶ Cubic crystals

TRANSMITTANCE

Grain size

glass J, spherical crystals, ~42% crystallized



$I(\lambda)$ dependence

Crystal size

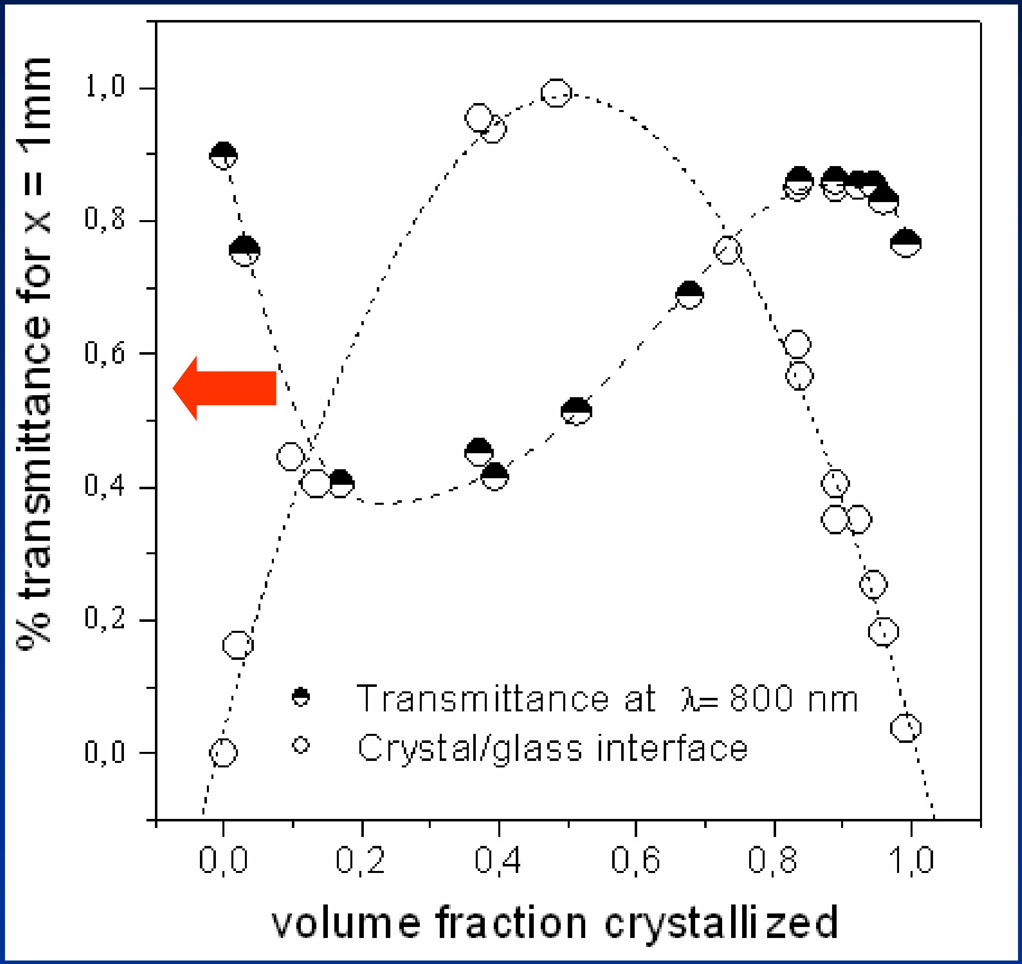
Affects P_2

Importance of thermal history

TRANSMITTANCE

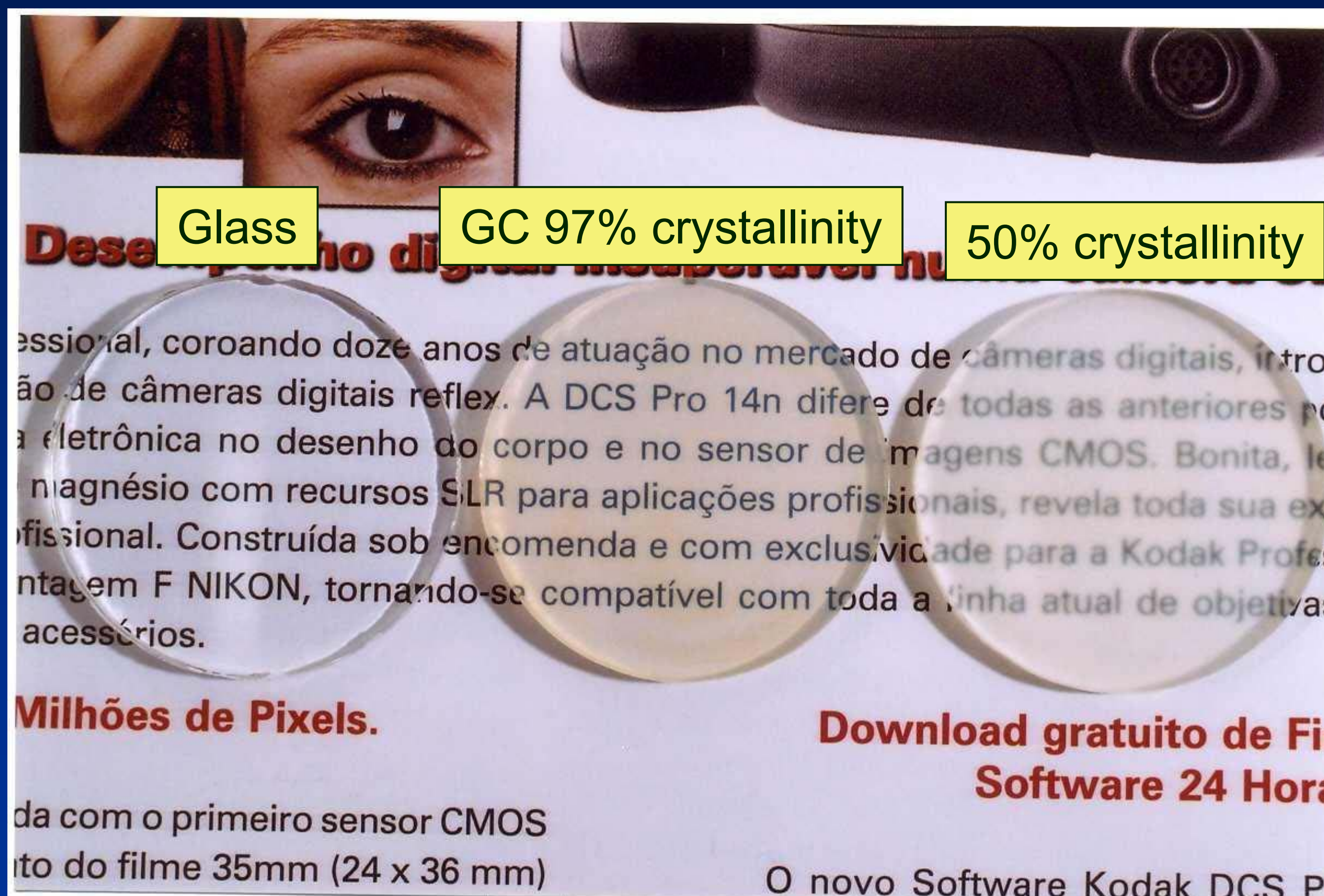
Degree of crystallinity

glass V8, cubic crystals (3-5 μm)

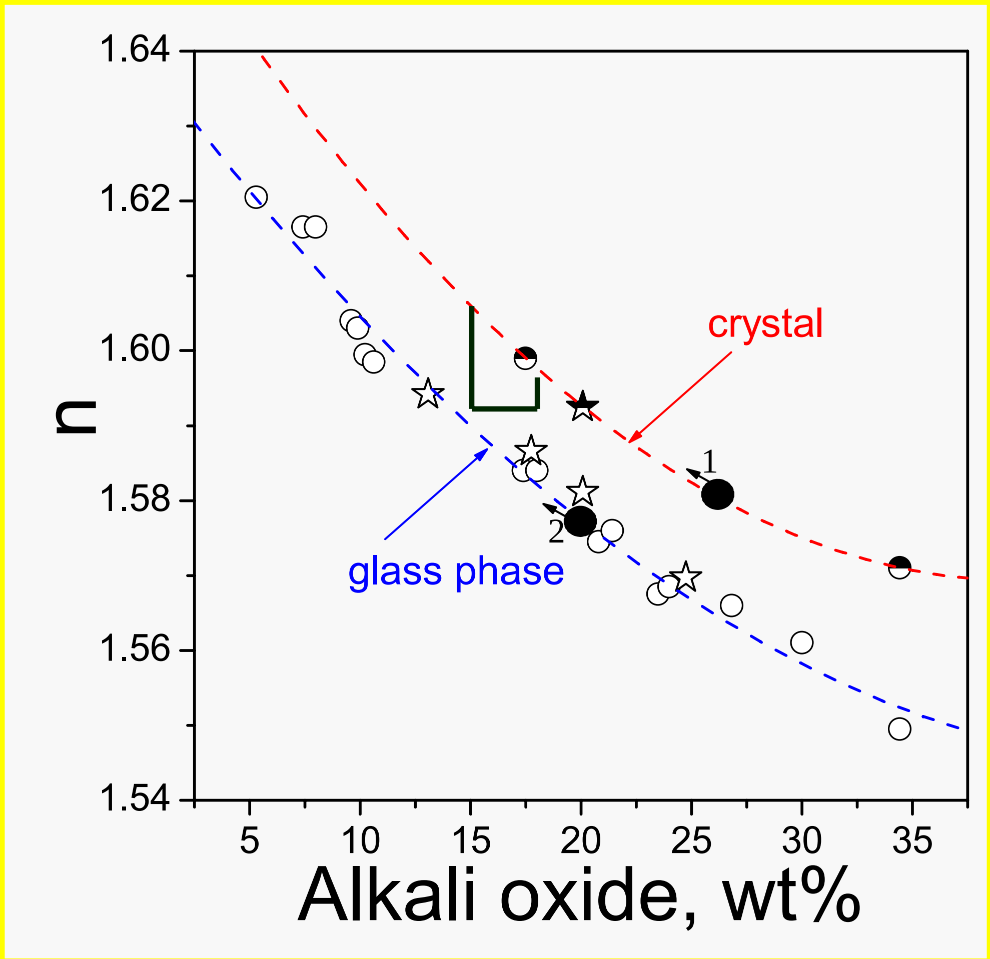


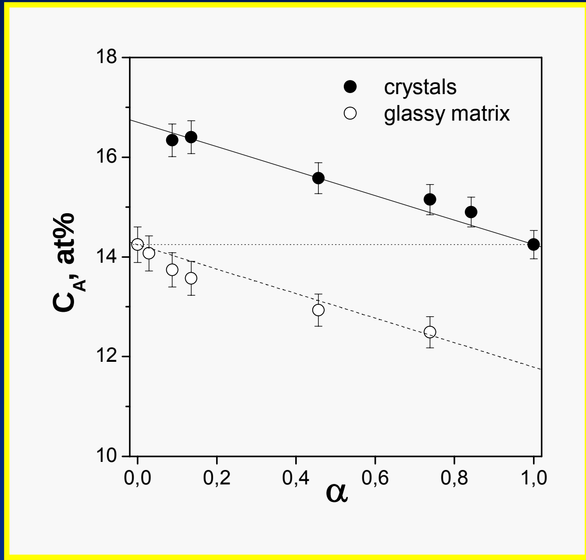
Glass V8 & T6, maximum transmission for ~ 95-97% OM crystallinity

The beasts! Transparency of 4 mm thick specimens



DISCUSSION





alkali content in crystals

30% > glassy matrix

EDS measurements

DISCUSSION

High crytallized fraction

↓

reduced crystal / glass interface

↓

Simultaneous variations of the glass-matrix and s/s-crystal compositions during crystallization

↓

refractive indexes of crystal and glass verge

↓

Main reasons for improved transparency in these new TGC

- Mechanical behaviour of HCHTGC

- A new, specially designed, method of impact testing!

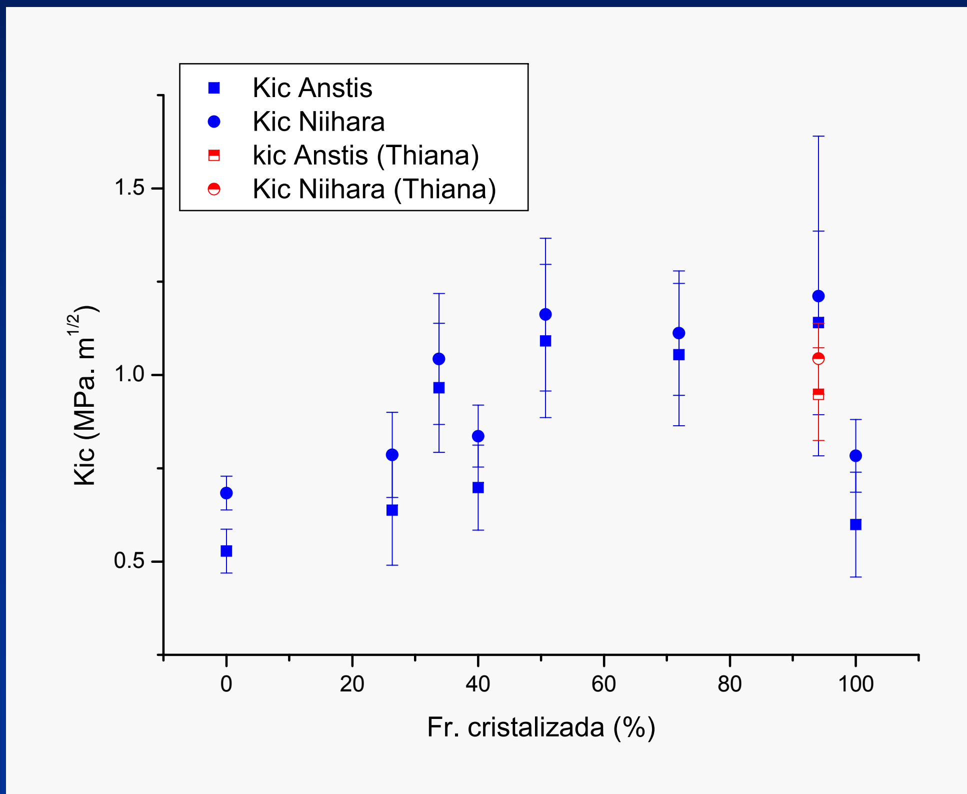
Impact testing of glass
Courtesy of Leo Siiman, Creol/ UCF

- Don’t try this experiment in your lab!

Kic versus volume fraction crystallized

Average grain size
from 3 to 6 um

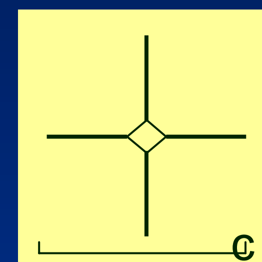
E_{glass}
71 GPa



E_{cr} ~105

Anstis

$$K_{IC} = 0.016\left(\frac{E}{H}\right)^{\frac{1}{2}}\frac{F}{c^{\frac{3}{2}}}$$



Nihara

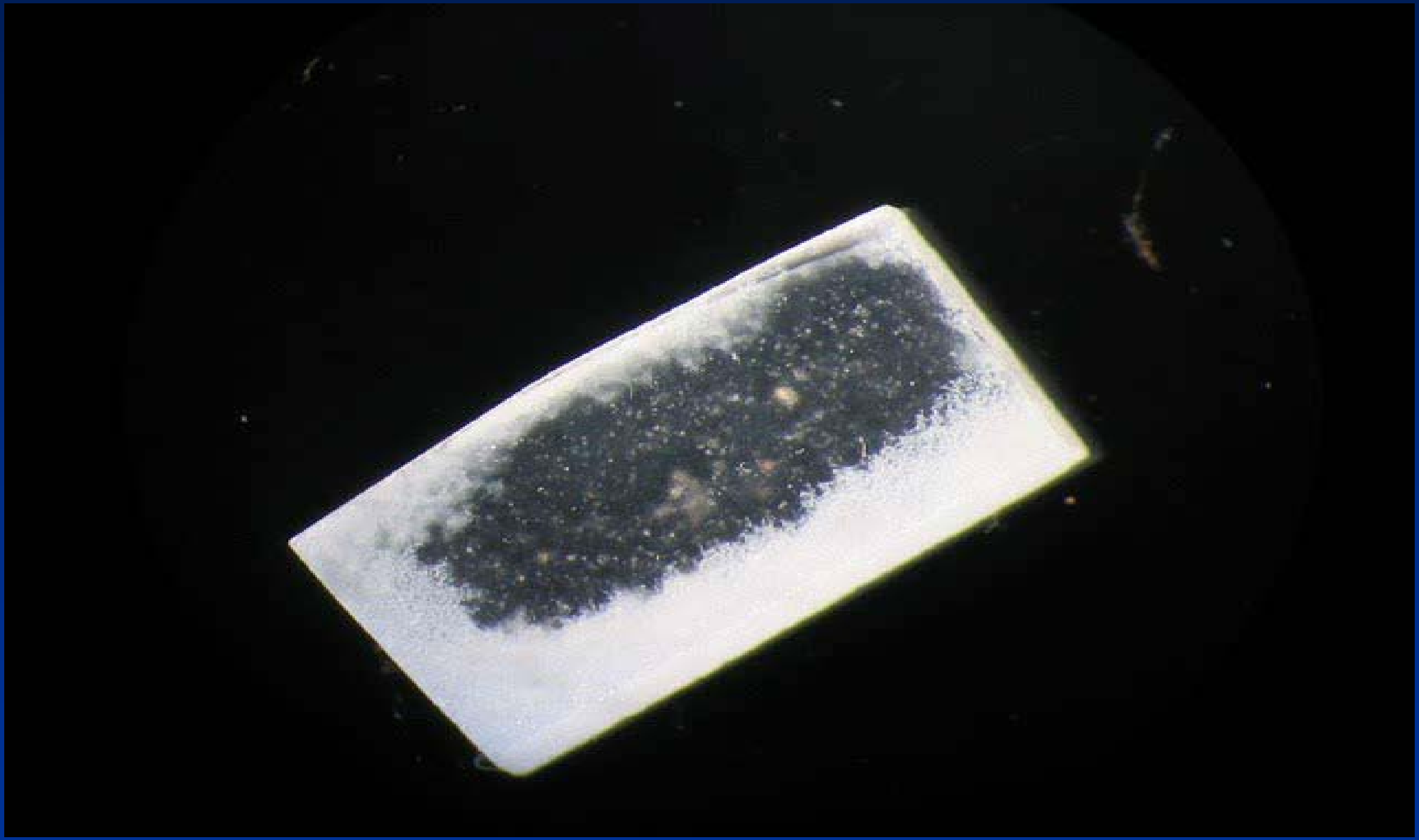
$$kic = 0{,}035\left(\frac{l}{a}\right)^{-\frac{1}{2}}\left(\frac{H}{E\phi}\right)^{-\frac{2}{5}}\left(\frac{H\sqrt{a}}{\phi}\right)$$

ϕ~3,
a,l,c [um]

- Why do the transparency and impact strength drop significantly for > 97% crystallinity?

SPONTANEOUS CRACKING for > 97% crystallinity!

accelerated 300X



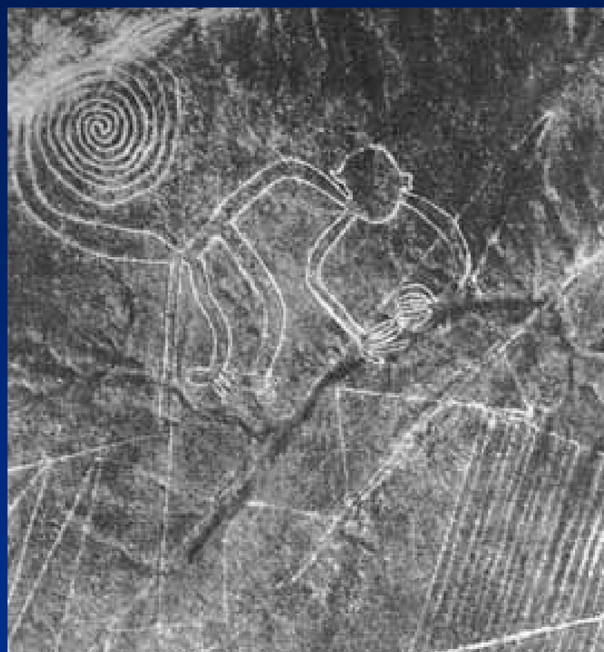
CONCLUSIONS

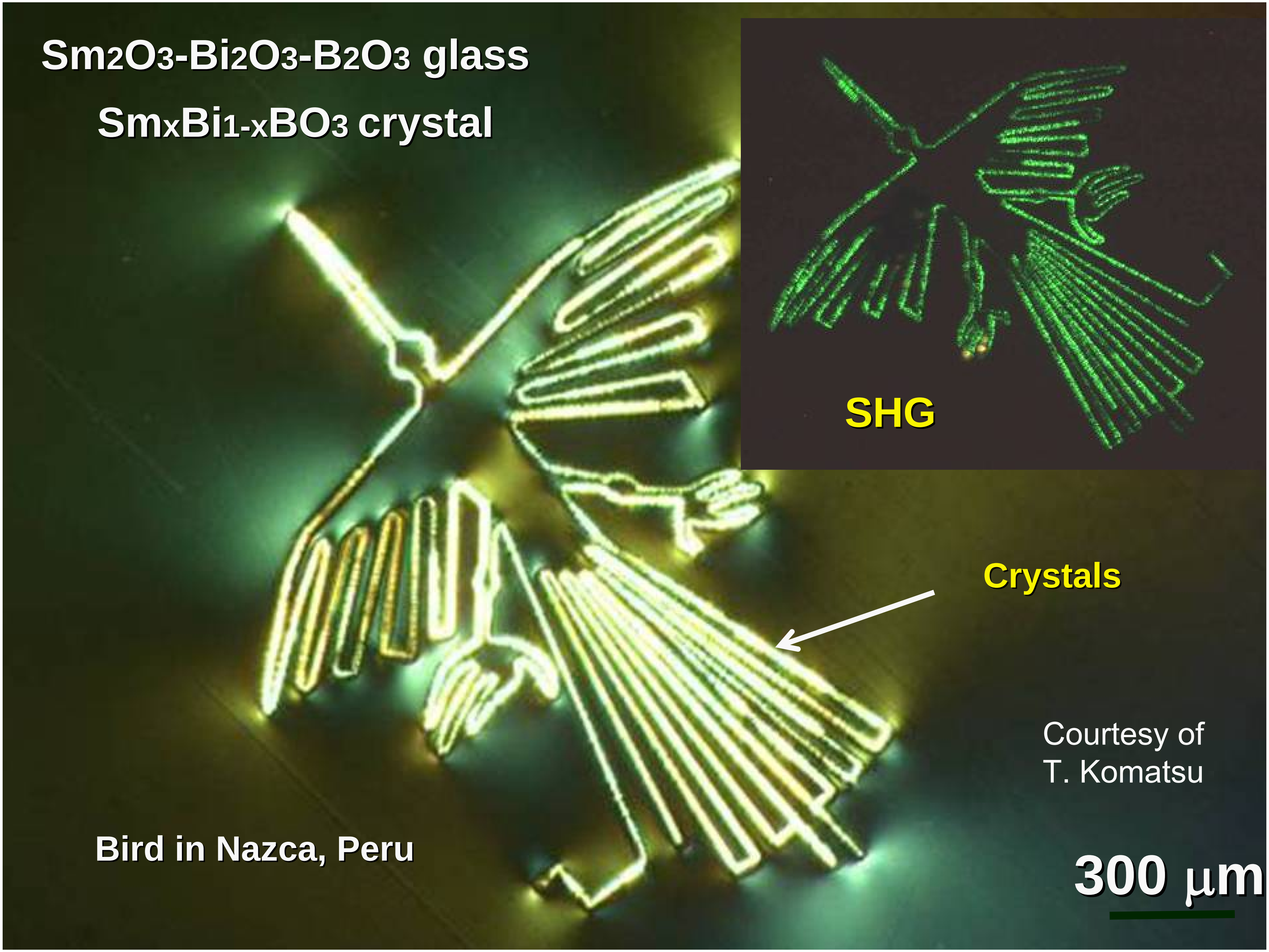
New

type of TGC ➡

- highly transparent in the visible ~ 90% for 1mm
- nm to μm grain size
- up to 97% crystallized volume fraction
- chemical durability OK
- good mechanical properties, which can probably be much improved by ion-exchange.
- can be drawn into fibers
- luminescence ? doping with Cr and RE ions should be tested...

On the origem of misterious biomorphs and geoglyphs in Nazca, Peru, 200 B.C.





Sm_2O_3-Bi_2O_3-B_2O_3 glass
$Sm_xBi_{1-x}BO_3$ crystal
SHG
Crystals
Courtesy of T. Komatsu
Bird in Nazca, Peru
300 μm

VITREOUS MATERIALS LAB, UFSCar, São Carlos BRAZIL

Thank you!