

LAMAV

Vitreous Materials
Laboratory



Transparent *glass - ceramics*

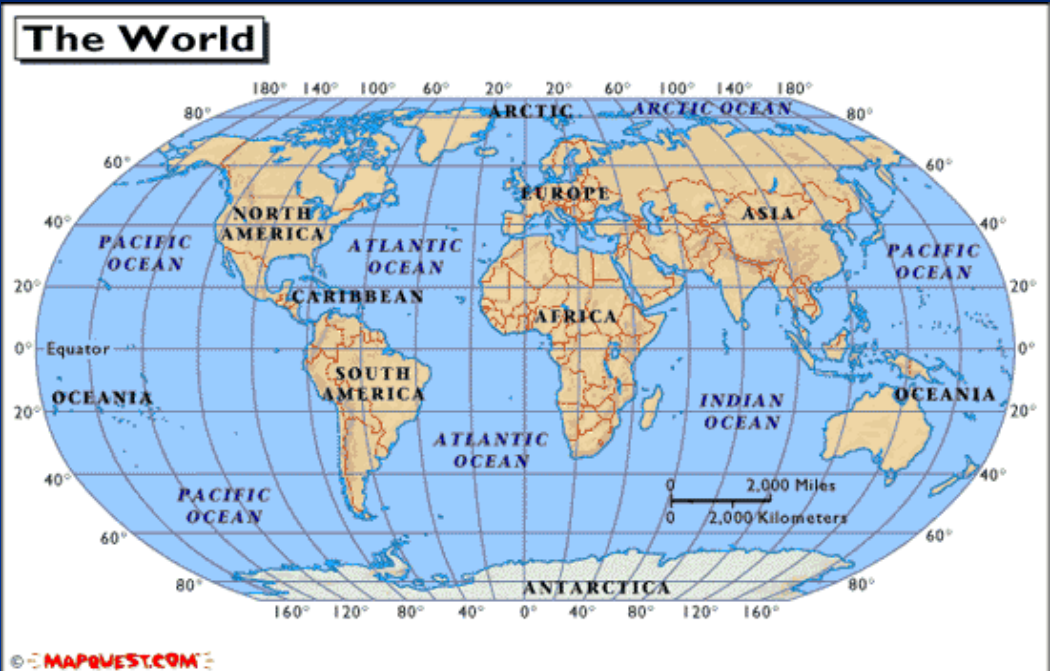
Edgar D. Zanotto

Vitreous Materials Lab

Federal University of São Carlos, Brazil

www.lamav.ufscar.br

Presented at the IMI-NFG US-Japan Winter School , Jan 14, 2008 and
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glass research community; Available at: www.lehigh.edu/imi



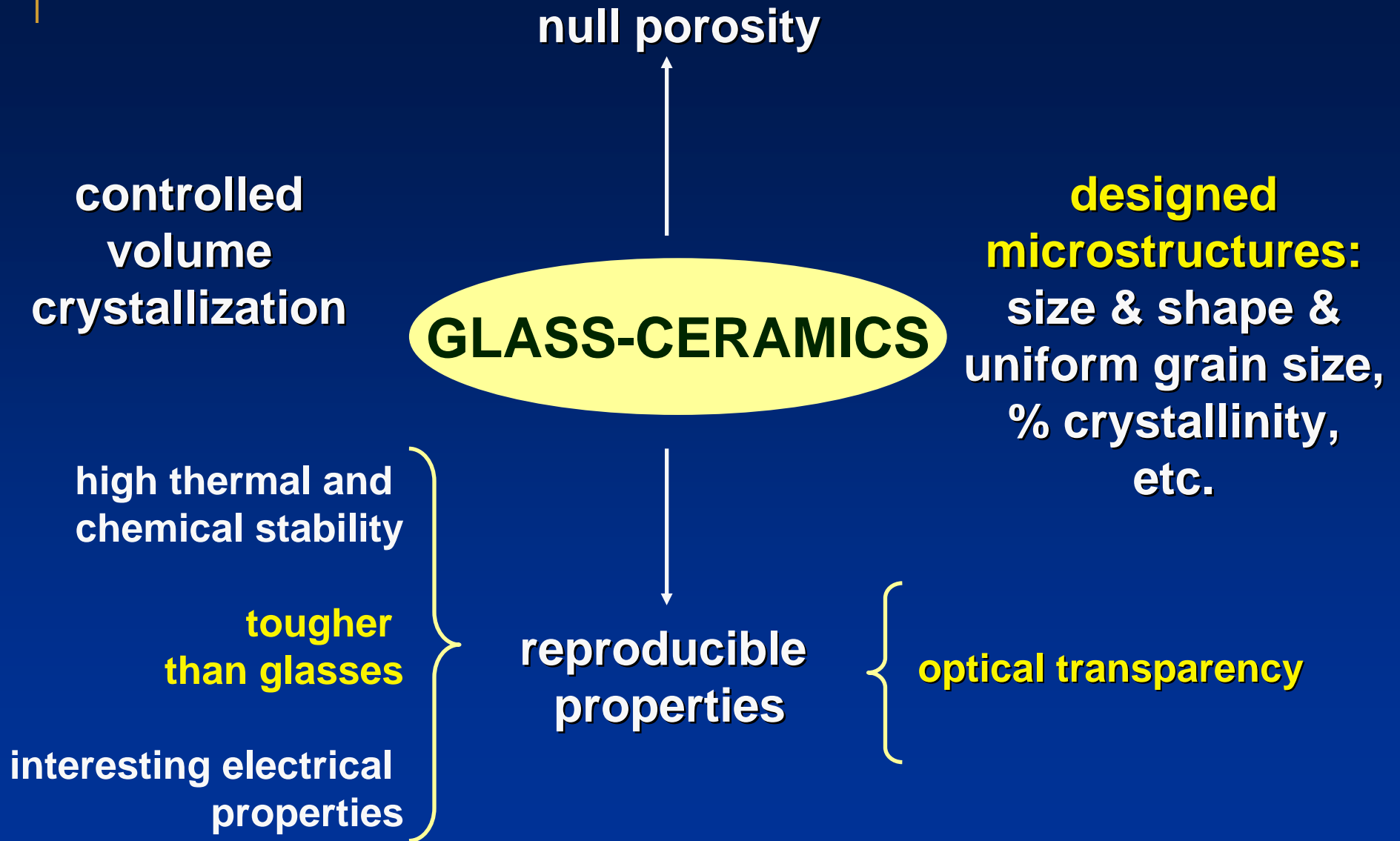
OUTLINE

- 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



INTRODUCTION

Applications of transparent glass-ceramics

Thermo-mechanical

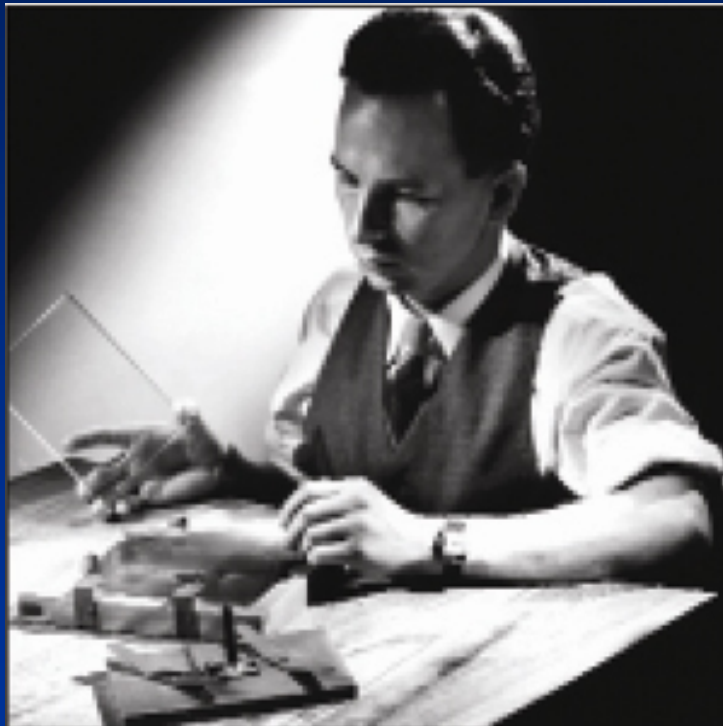
Cooking ware
Fire resistant plates
Security windows
Telescope mirrors...

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

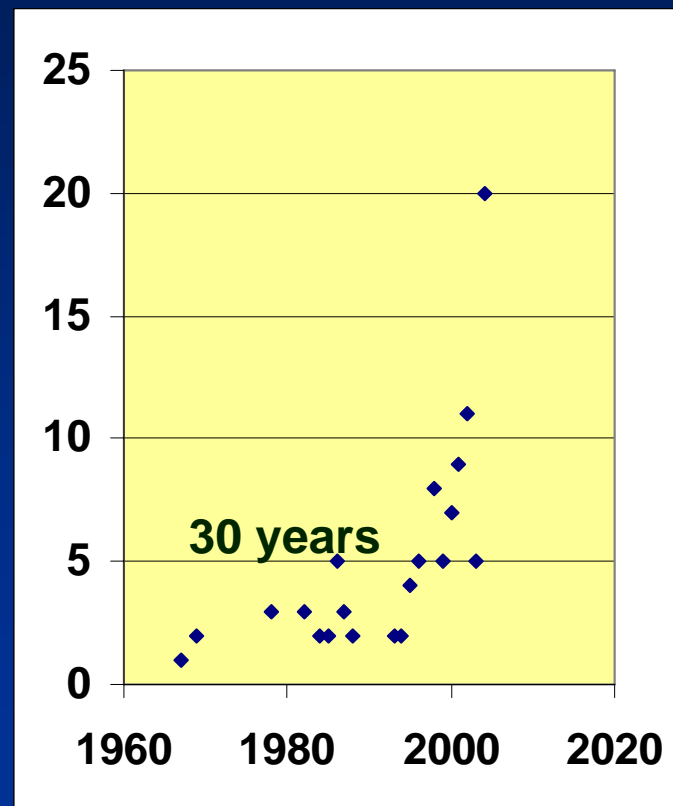
LITERATURE REVIEW (TGC title)

<u>YEAR</u>	<u>112 ISI papers</u>
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

- B-quartz ss
- B-eucryptite
- 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)

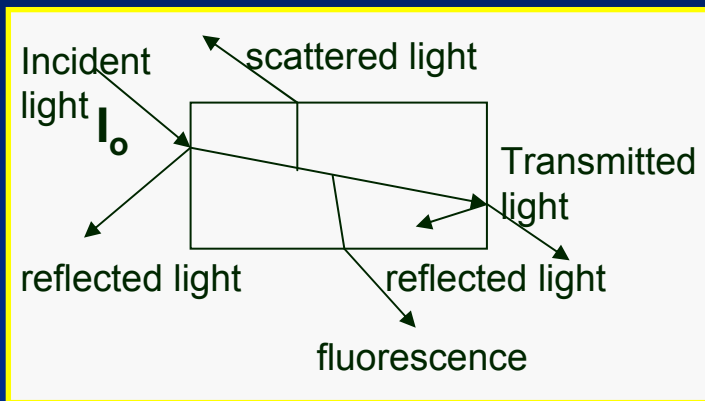
THEORY

Light attenuation

atomic absorption (β)

scattering (S)

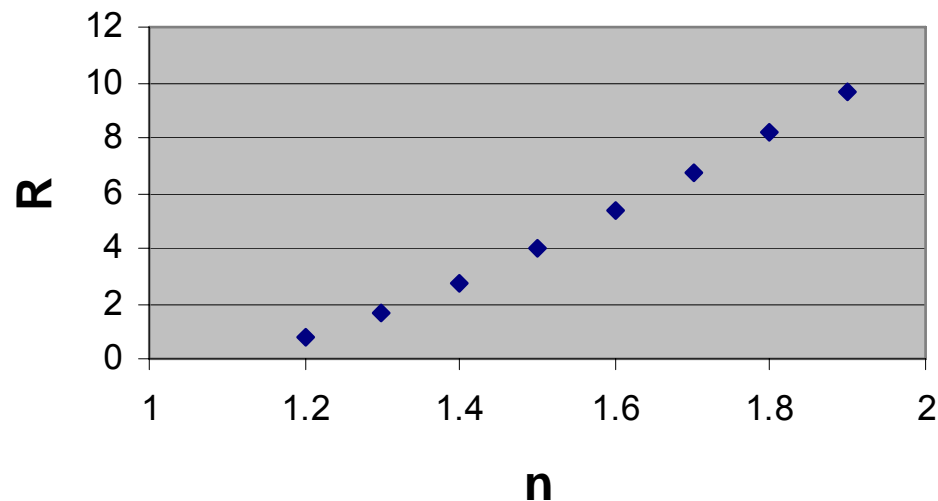
+ surface reflection (R)



$$I = I_0 (1 - R)^2 \exp(-(\beta + S)x)$$

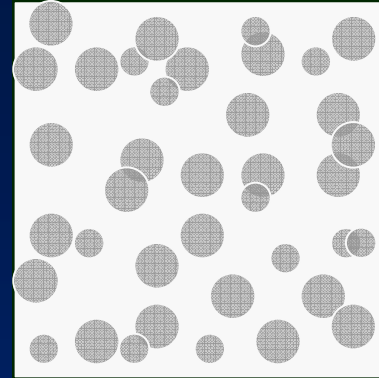
$$R = \left(\frac{n - 1}{n + 1} \right)^2$$

Reflection losses (%)



Conditions for transparency

Transparent glass-ceramics



crystal size \ll wavelength of light

Basic requirements

low birefringence

$$n_{\text{glass}} \approx n_{\text{crystal}}$$

Examples of commercially mature TGC

Corning's VISION

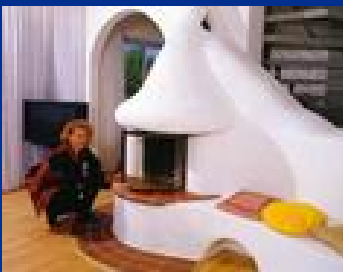


VLT 8.2 m Zerodur mirror on its way to Paranal Observatory, Chile, Dec. 97/ Schott



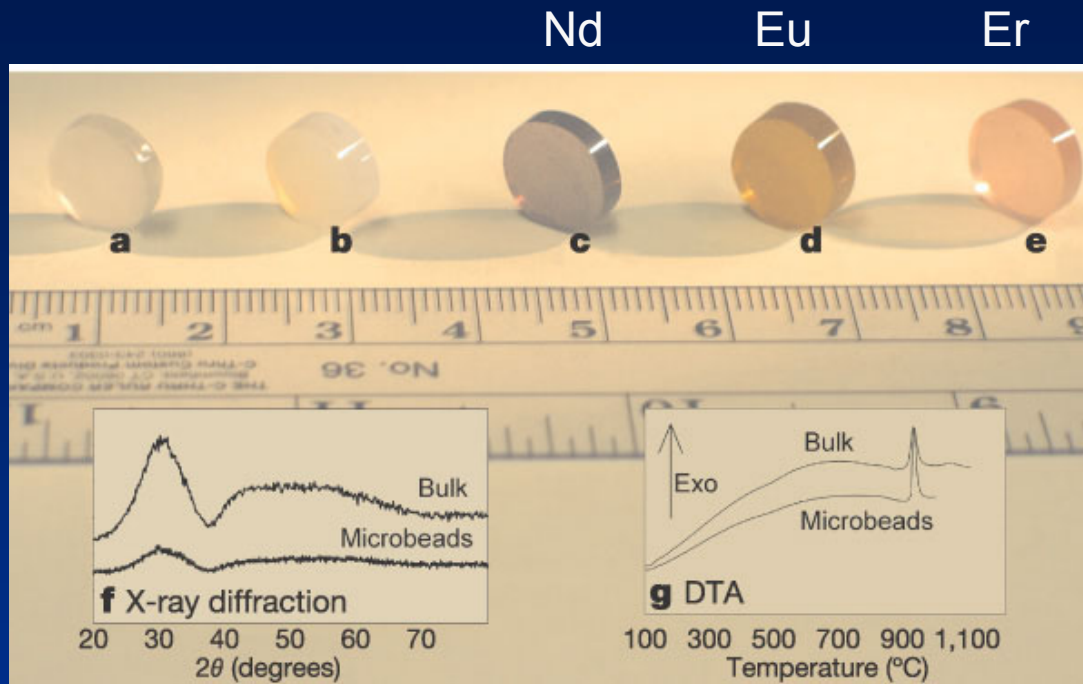
ROBAX – Schott
NEOCERAM – NIPPON
KERAGLASS- Corning/ St. Gobain

CERAN- Schott

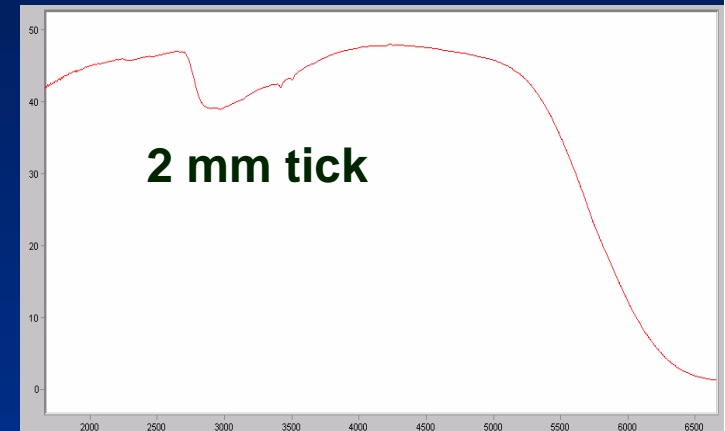


NEW
TRANSPARENT GC
(yet on the development stage)

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

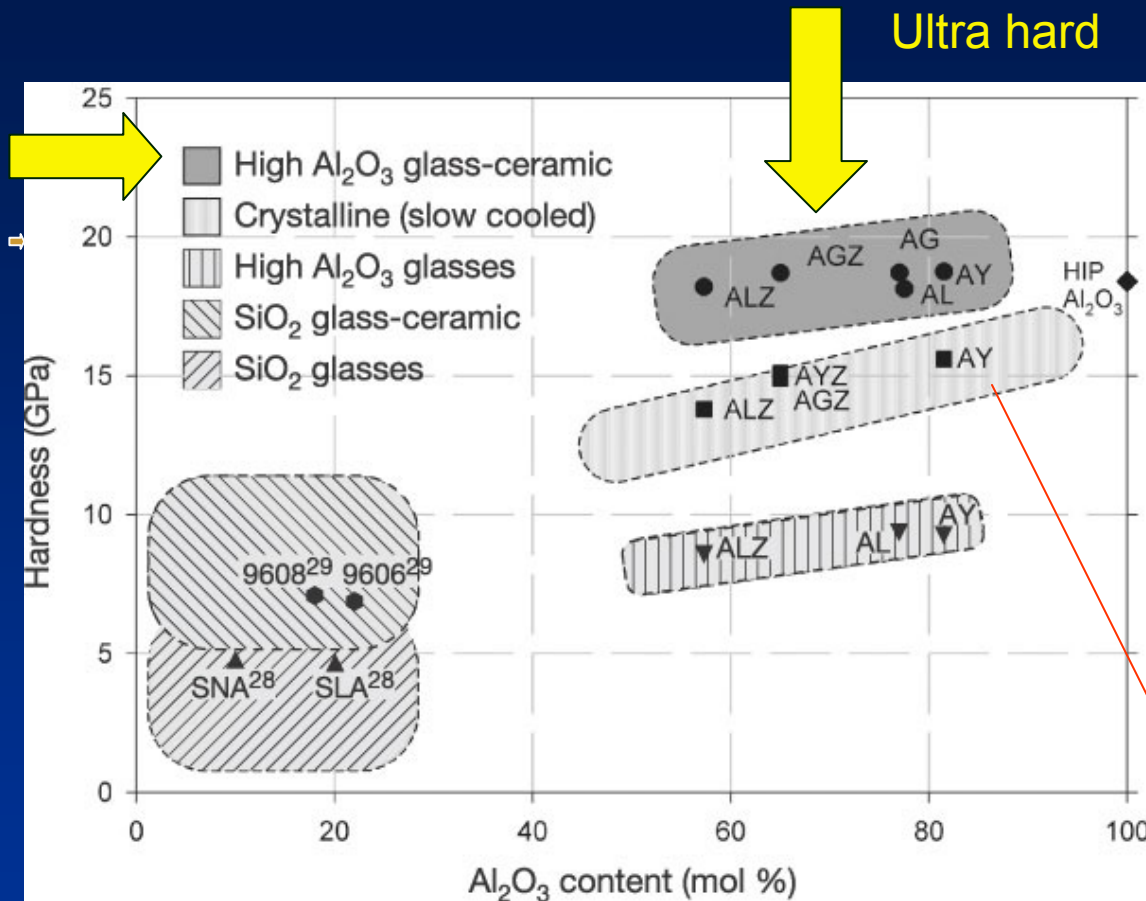


50-90% Al₂O₃

a, b: no dopants; c 5wt% Nd₂O₃; d 5wt% Eu₂O₃; e 5wt% Er₂O₃.
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.

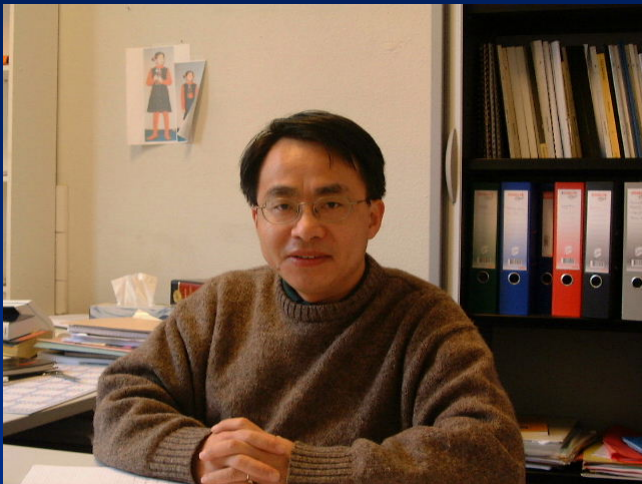
High alumina glasses and GC



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 chalcogen-sulfide glass-ceramics



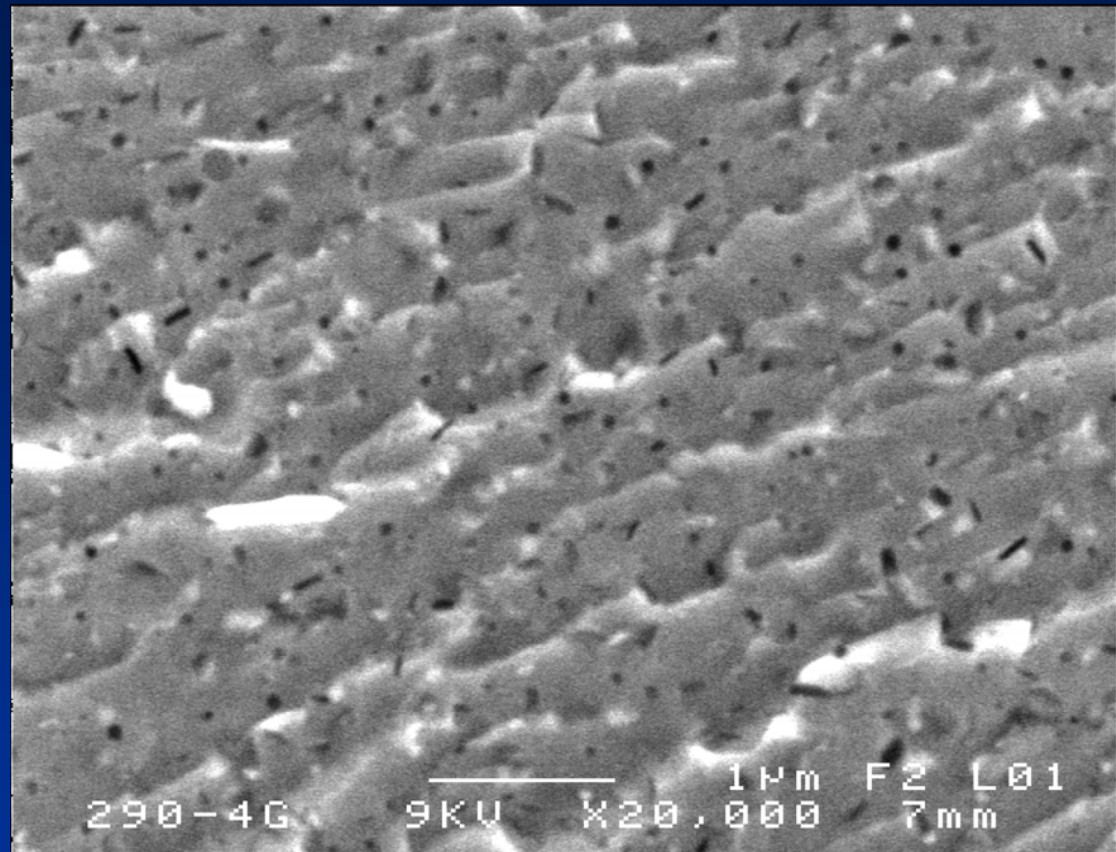
Ge-Sb-S-Cs-Cl glass with
CsCl crystals

X. Zhang et. al. , J. Non-
crystalline Solids 337 (2004)
130

**Lab. glasses and ceramics,
University of Rennes,
France**

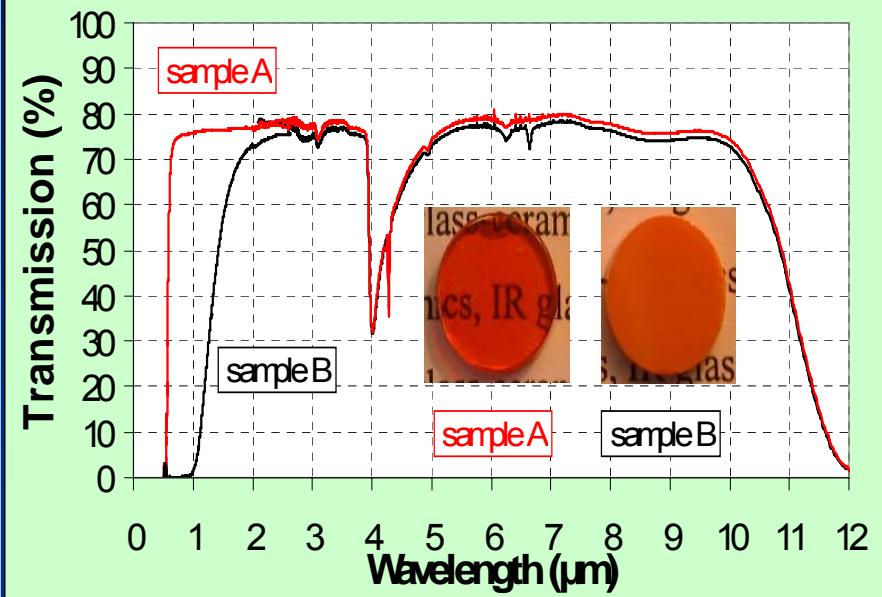
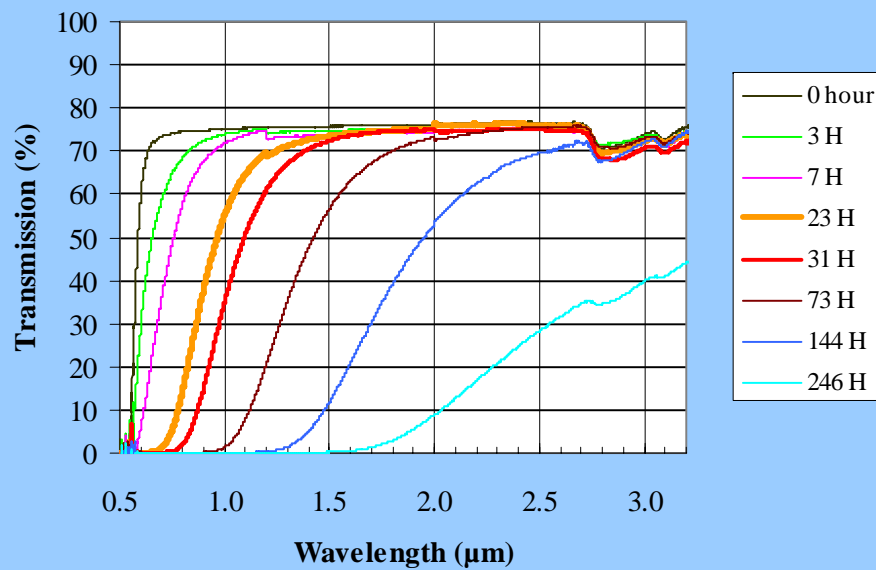
Typical microstructure of IR glass-ceramics

100nm CsCl
crystals



Zhang et. al.

IR transmission *versus* crystallinity

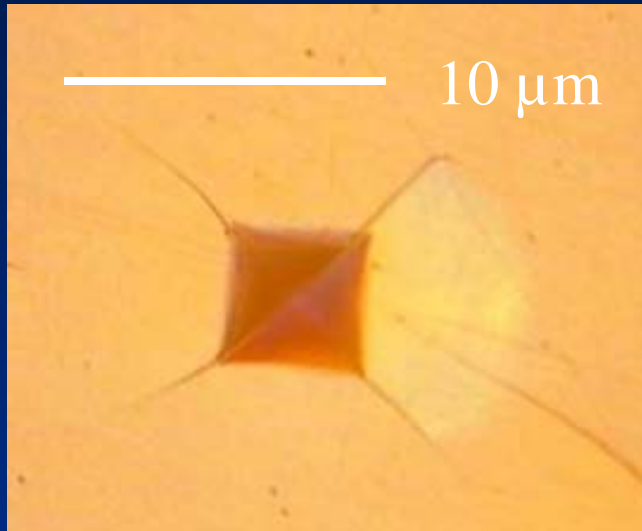


Zhang et. al.

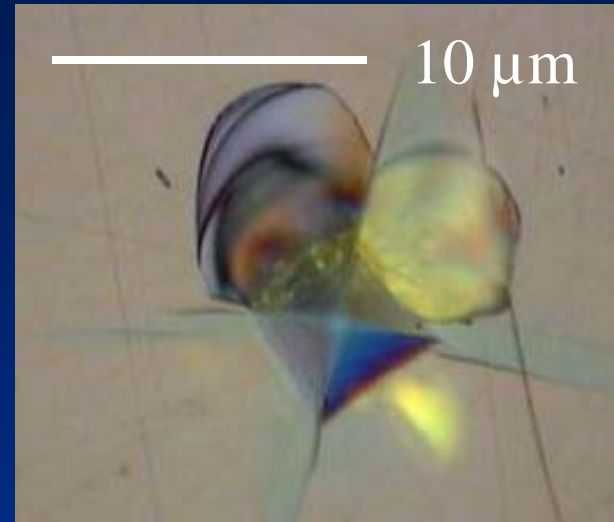
Night vision



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

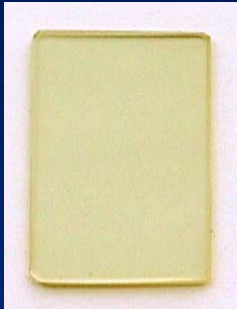
	Efficiency	Life
Incandescent Light Bulb	16 <i>lm / W</i>	1000 <i>h</i>
Fluorescent Lamp	80 <i>lm / W</i>	10,000 <i>h</i>
Today's white LED	60 <i>lm / W</i>	20,000 <i>h</i>
Future white LED	200 <i>lm / W</i>	100,000 <i>h</i>

Efficiently bright, broad spectrum, long-lifetime...

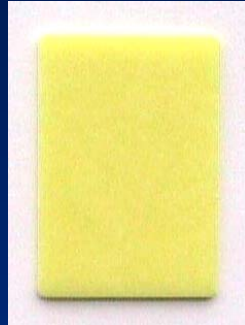
S. Tanabe et al.

YAG-GC from glass- microstructure

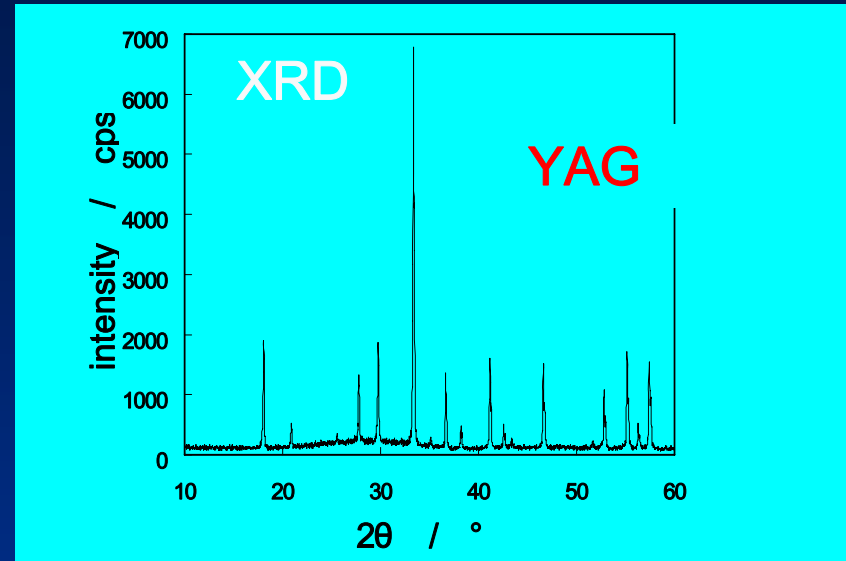
As-made



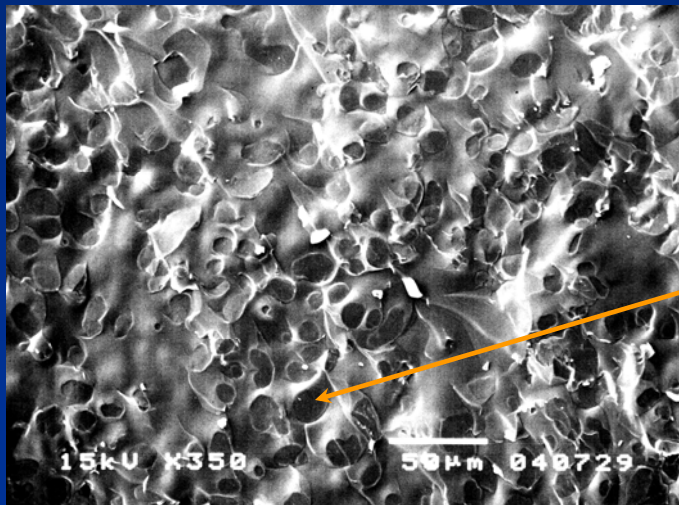
Cerammed



1cm



SEM



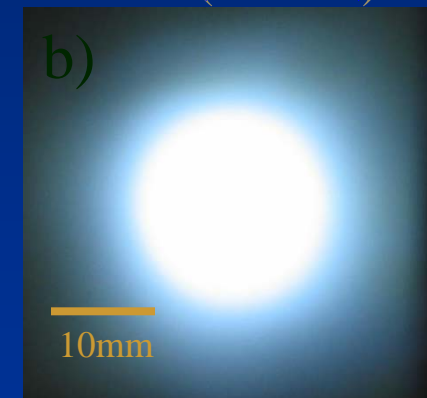
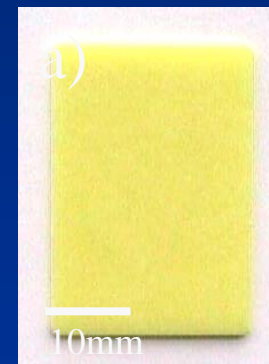
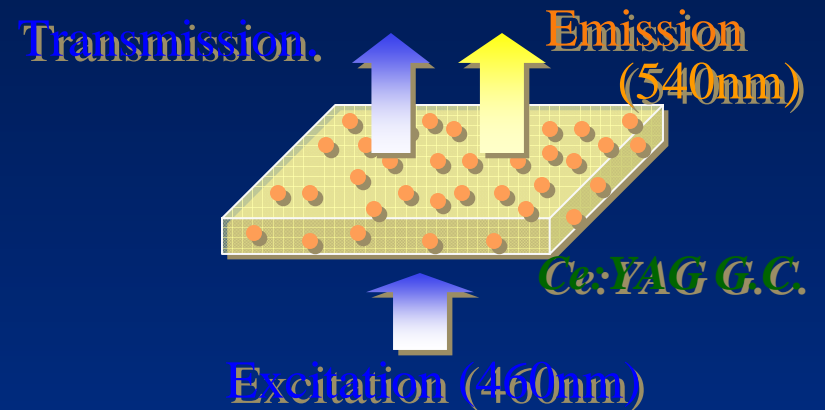
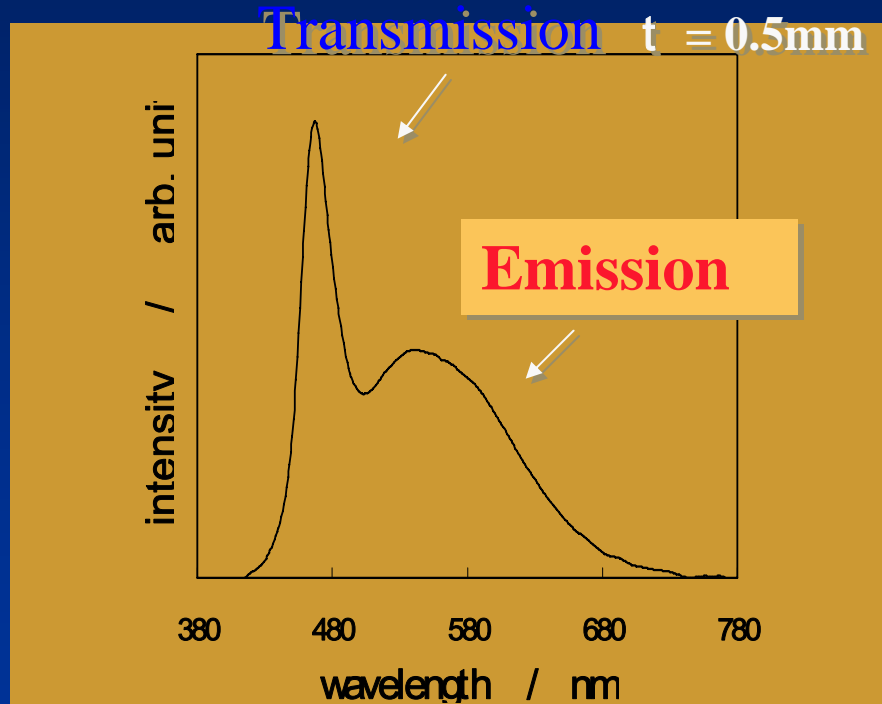
YAG
20µm

60%
Crystallinity
(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 \longrightarrow Crystallization

Writing of nonlinear optical/ferroelectric crystal dots and lines

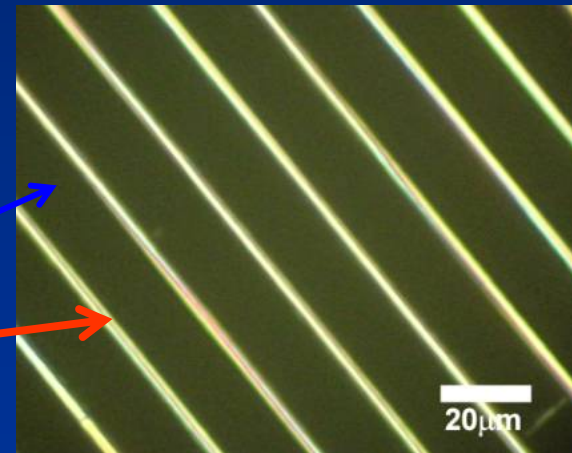
- $\text{Sm}_2\text{O}_3\text{-BaO-B}_2\text{O}_3 \rightarrow \beta\text{-BaB}_2\text{O}_4$
- $\text{Sm}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3 \rightarrow \text{Sm}_x\text{Bi}_{1-x}\text{BO}_3$
- $\text{Sm}_2\text{O}_3\text{-MoO}_3\text{-B}_2\text{O}_3 \rightarrow \beta'\text{-Sm}_2(\text{MoO}_4)_3$
- $\text{Sm}_2\text{O}_3\text{-K}_2\text{O-P}_2\text{O}_5 \rightarrow \text{KSm}(\text{PO}_3)_4$

$\text{Sm}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glass

$\text{Sm}_x\text{Bi}_{1-x}\text{BO}_3$ crystal

Power: 0.66W

Scanning speed: $10\mu\text{m/s}$



20,000
 J/cm^2

Polarization optical microscope



長岡技術科学大学

Komatsu

10Sm₂O₃.35Bi₂O₃.55B₂O₃ glass

T_g=474°C, T_x=574°C

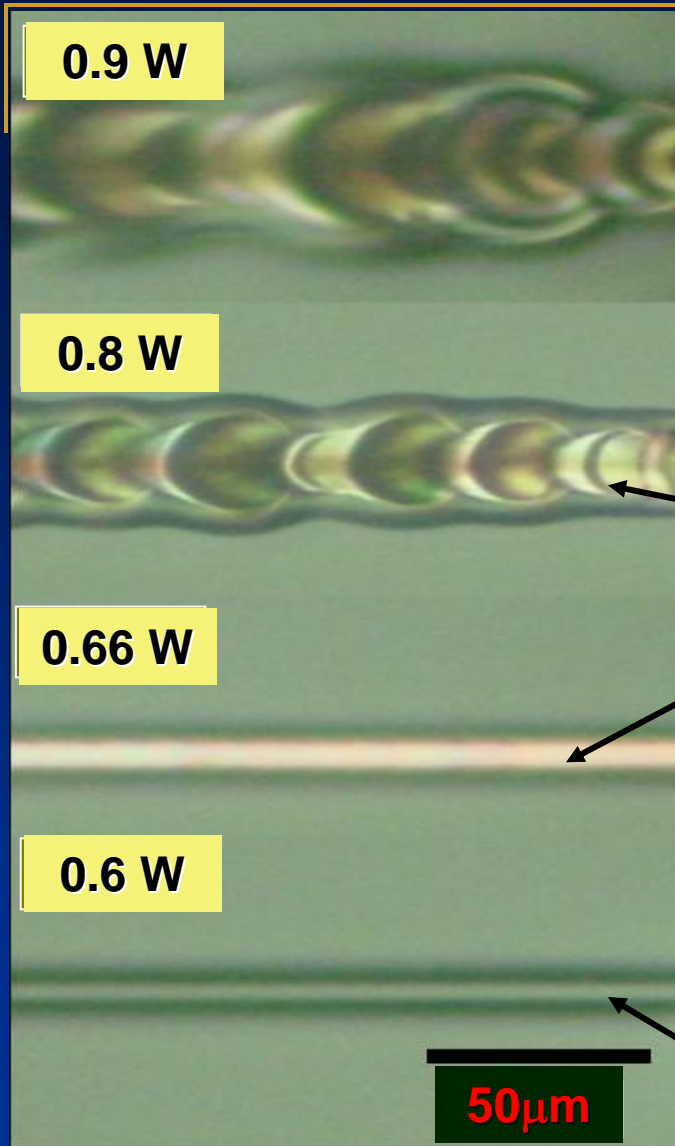
Sm_xBi_{1-x}BO₃

crystal

Temp. >> T_x

Temp. < T_x

Refractive index change



Laser crystallization in São Carlos

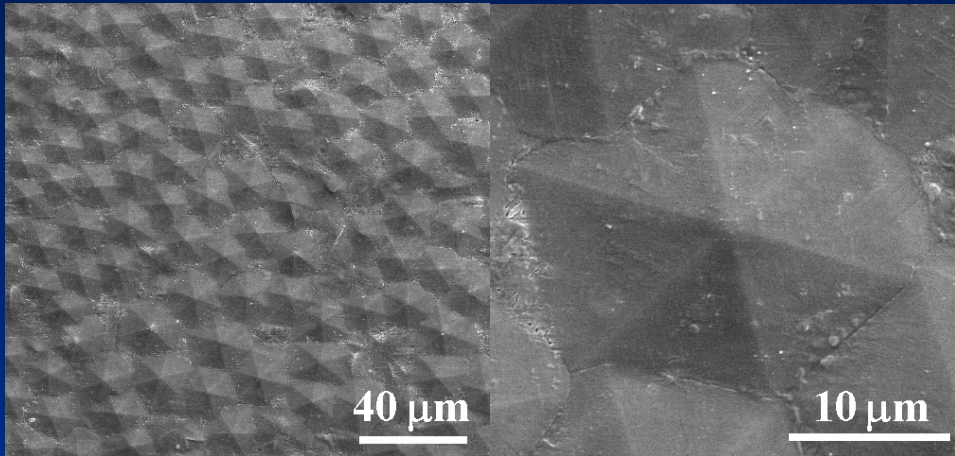
C. A. C. Feitosa, L. J. Q. Maia, A. L. Martinez,
A. C. Hernandez, **Valmor R. Mastelaro**,

IFQSC,
University of
São Paulo, São
Carlos, Brazil

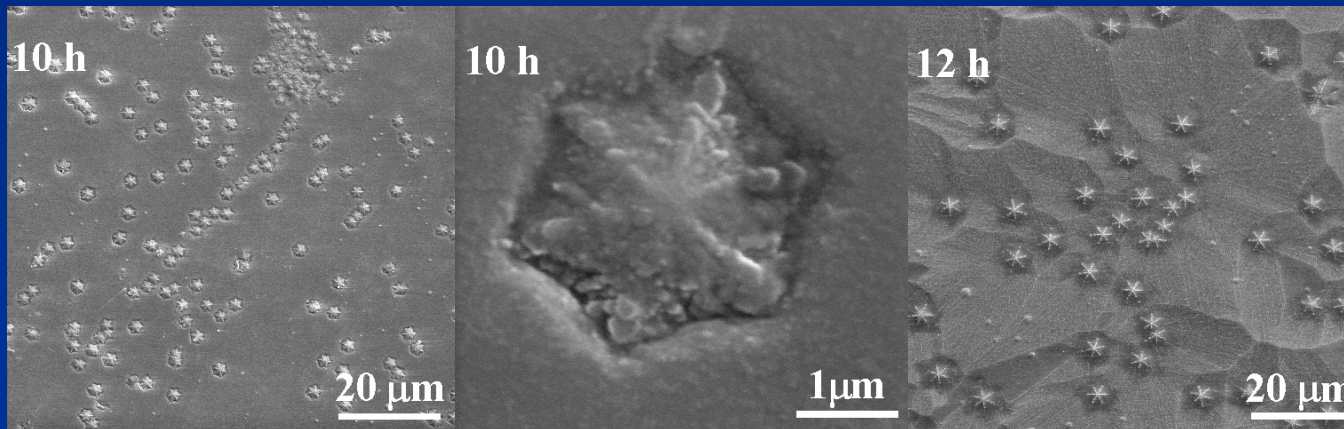


40BaO - 45B₂O₃ - 15 TiO₂ (BBT)

Microstructures from two crystallization processes

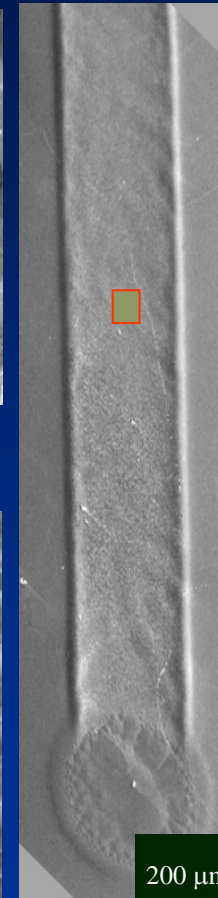
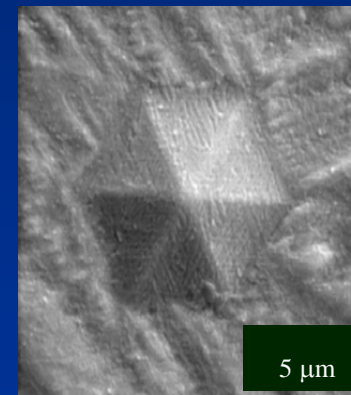
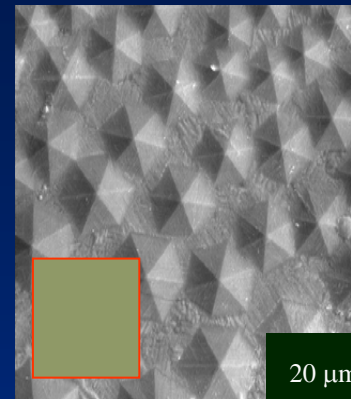
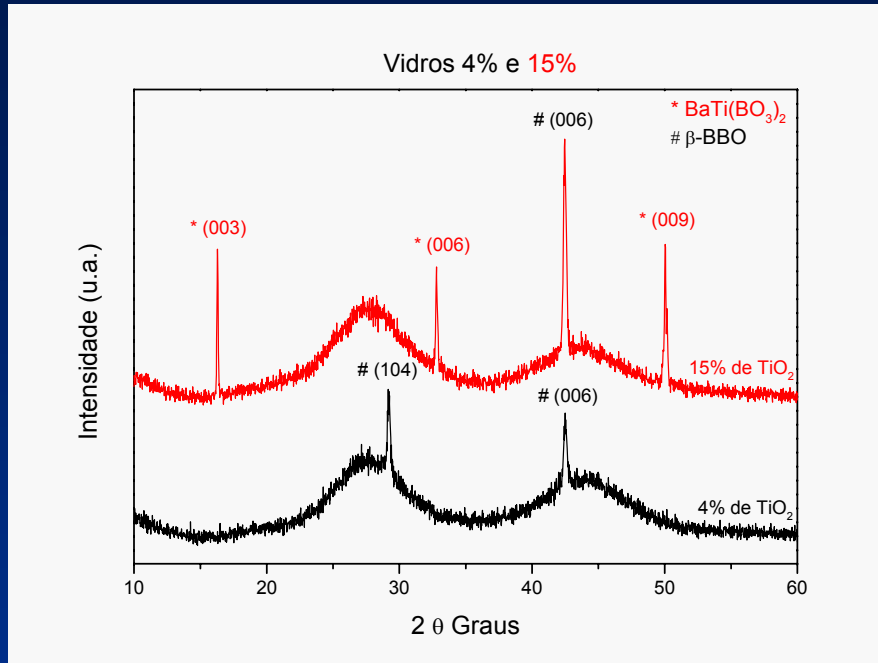


BBT glass after irradiation with CO₂ laser ($\lambda = 10.6 \mu\text{m}$) 4 min, 40 W/cm².
= 10,000 J/cm²
Glass at 300°C ($T_g = 580 \text{ }^\circ\text{C}$)



BBT GC in resistive furnace at 620°C.

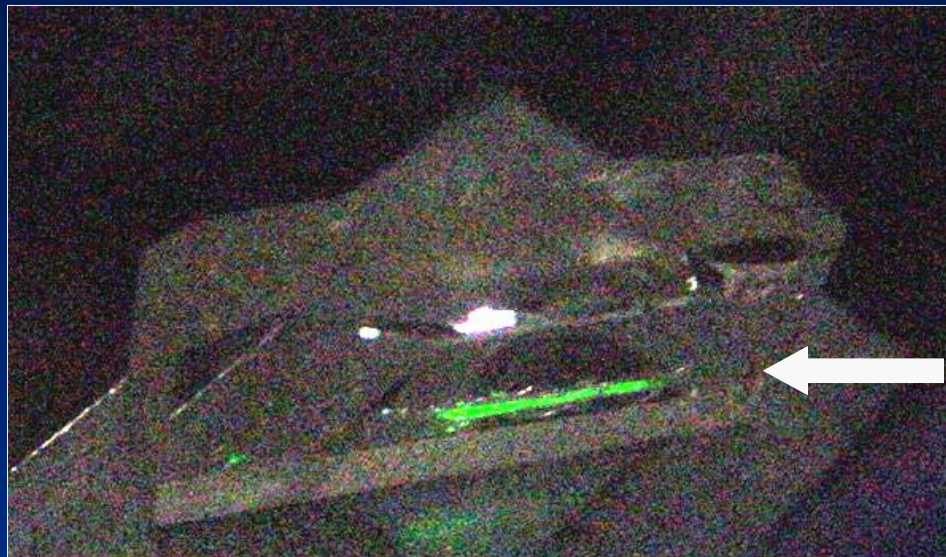
Surface crystallization of BBT glass



It is possible to produce polycrystalline lines.

Details; crystals within the line and diffraction pattern

SHG in partially crystallized BBT glass



Mastelaro et. al.

Laser beam
Nd:YAG ($\lambda = 1064 \text{ nm}$)



Second harmonic generation 

PTR Glasses

Oxy fluor bromide glasses

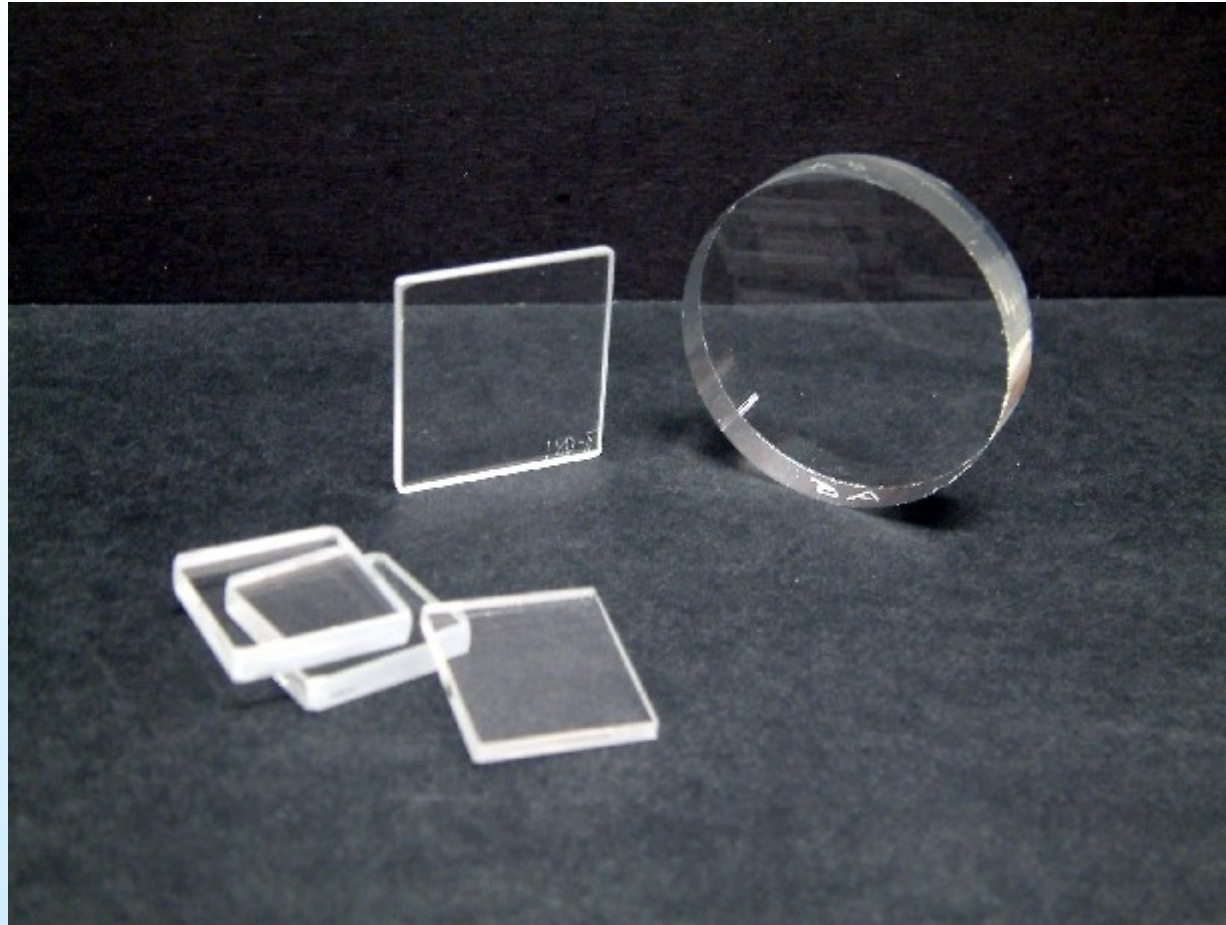
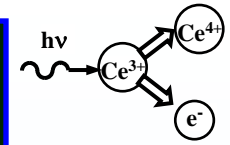
S.D. Stookey et al. (1954) – Corning, USA

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**



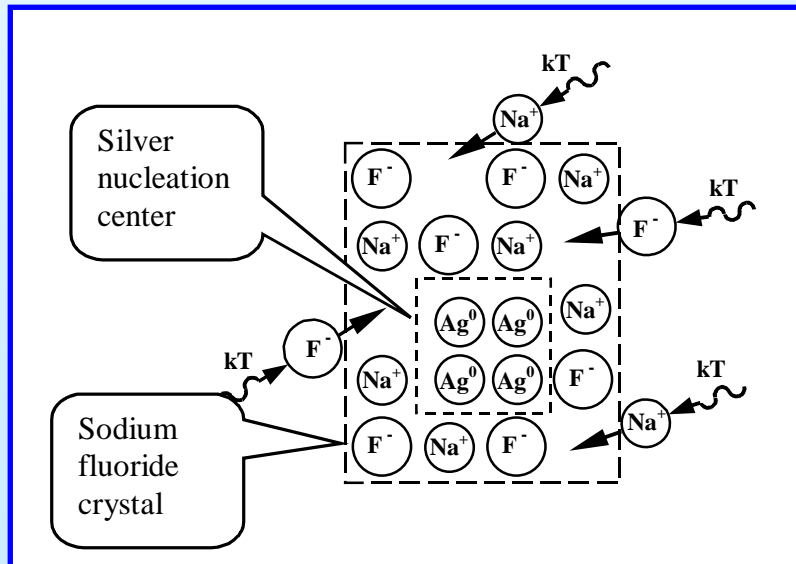
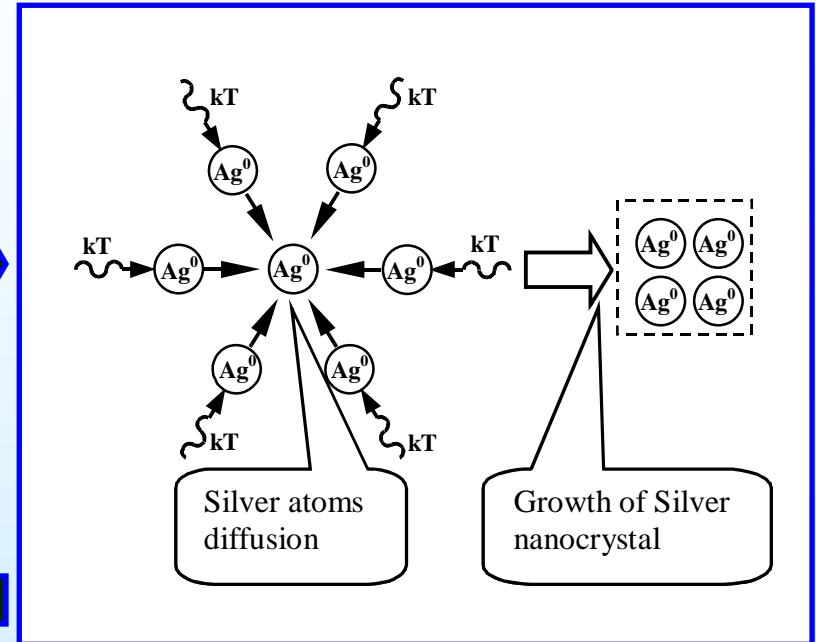
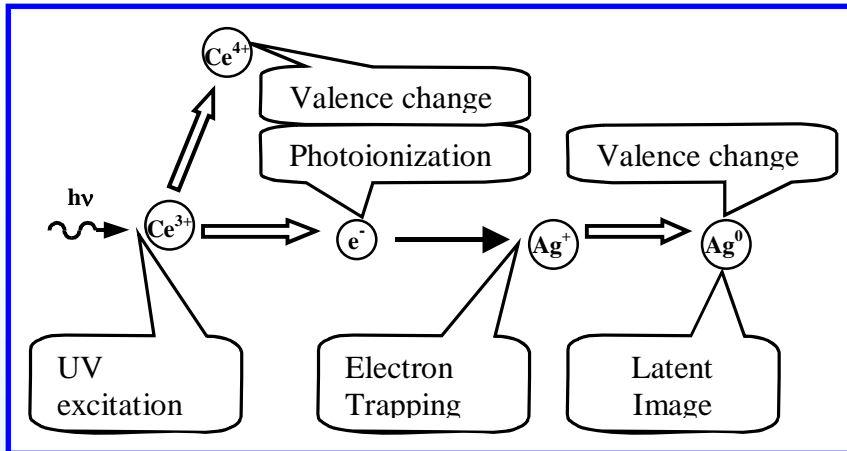
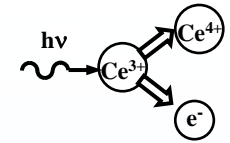
PTR glass is a F-Br sodium-zinc-aluminum-silicate glass doped with Ag, Ce, Sn and Sb



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

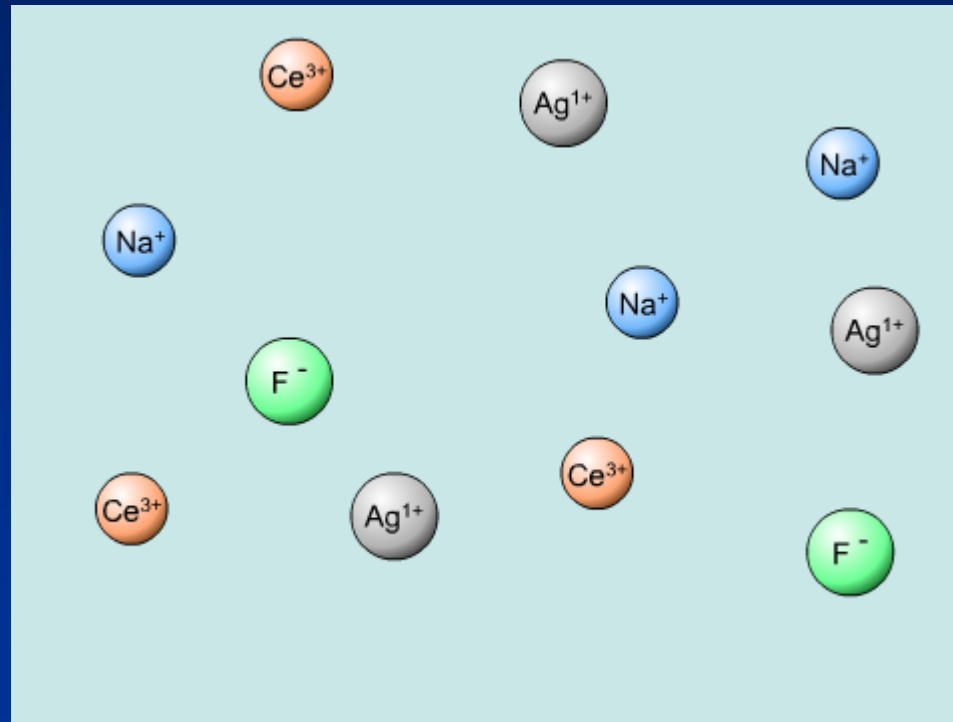


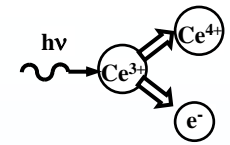
Mechanism of photo-thermo-crystallization



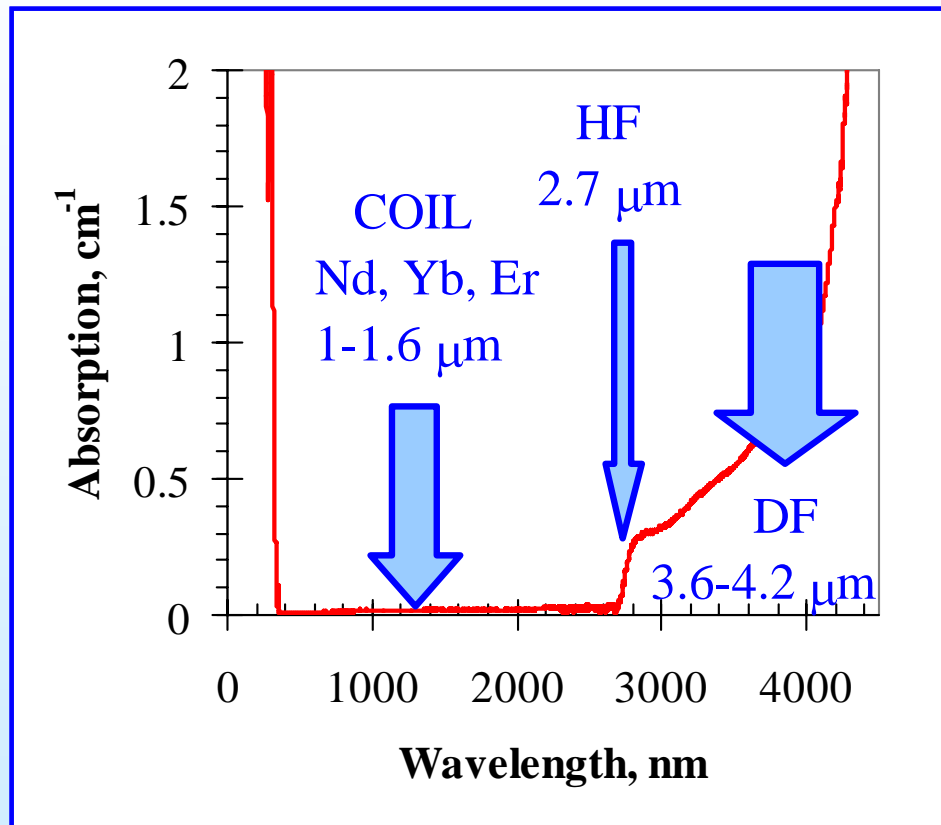
3D image (hologram) of object is transformed to the phase pattern (refractive index variations) caused by selective NaF crystal distribution in accordance with the UV intensity distribution in glass interior.

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.

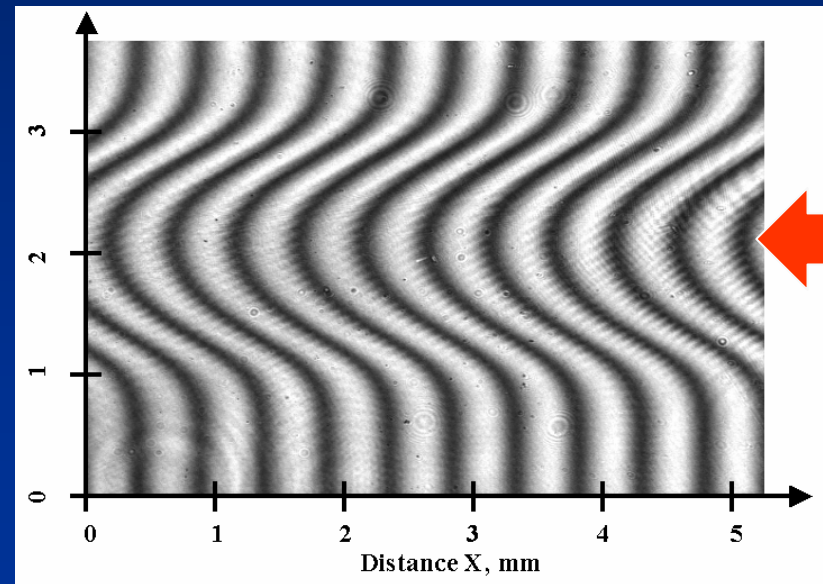
Leon Glebov, who had served as director of the Vavilov Institute during the tumultuous period prior to the dissolution of the USSR, was recruited to UCF in 1995 by M.J. Soileau, current vice president for research who at that time was director of CREOL. At the time Glebov was participating in the U.S. 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.

Leon,
To develop Fotalite®
1) Make exposure
2) Ramp to 530°C at any rate
3) Hold 45 min.
4) Cool below 400°C at any rate
5) Ramp to 570°C at any rate
6) Hold 45 min.
7) Cool furnace rate
Joe Pierson
607-974-3458



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**

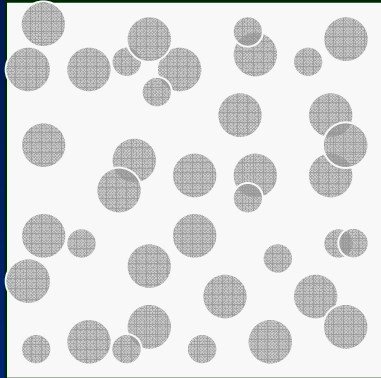
decreases Δn

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):

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

$$P_1 = (1-R)^2$$

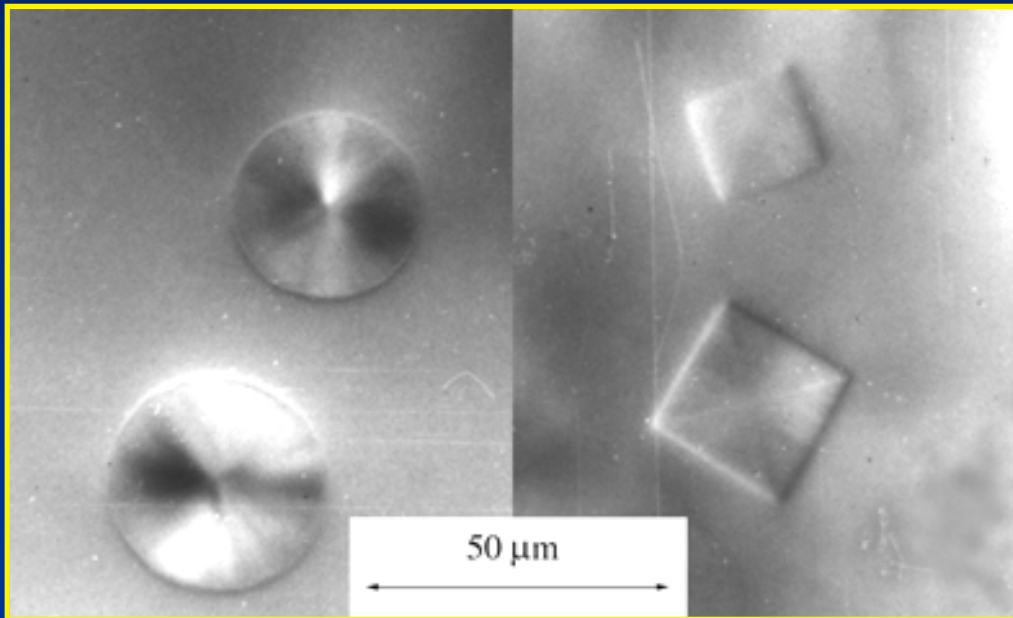
$$P_2 = (\beta+S)$$

MICROSTRUCTURES

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

Their morphology can vary from

J, spherical to **V8**, cubic



T = trace element

A = alkali

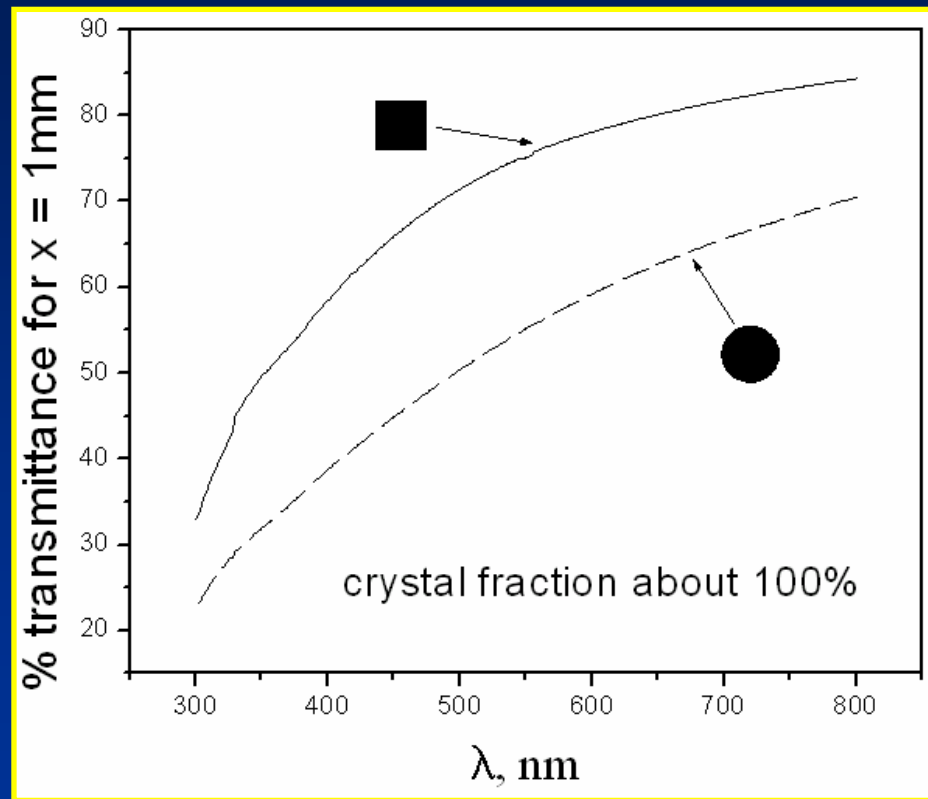
AE = alkaline earth

GF = Si, P, B

TRANSMITTANCE

Morphology

Distinct crystal shapes \longrightarrow Different transmittances



V8, cubic 5-6 μm
J, spherical 7-8 μm

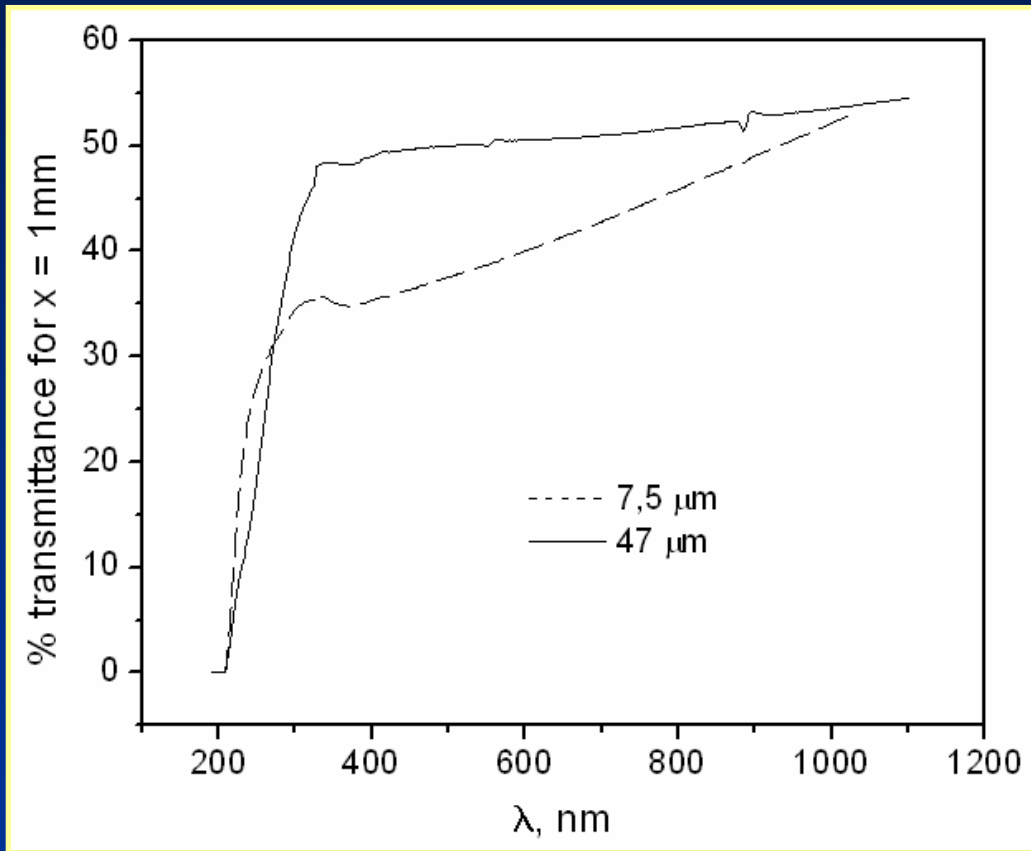
crystal/crystal
Interfaces are
quite different for
spherical and
cubic crystals

Best transmittance \longrightarrow Cubic crystals

TRANSMITTANCE

Grain size

glass J, spherical crystals, ~42% crystallized



$I(\lambda)$ dependence



Crystal size



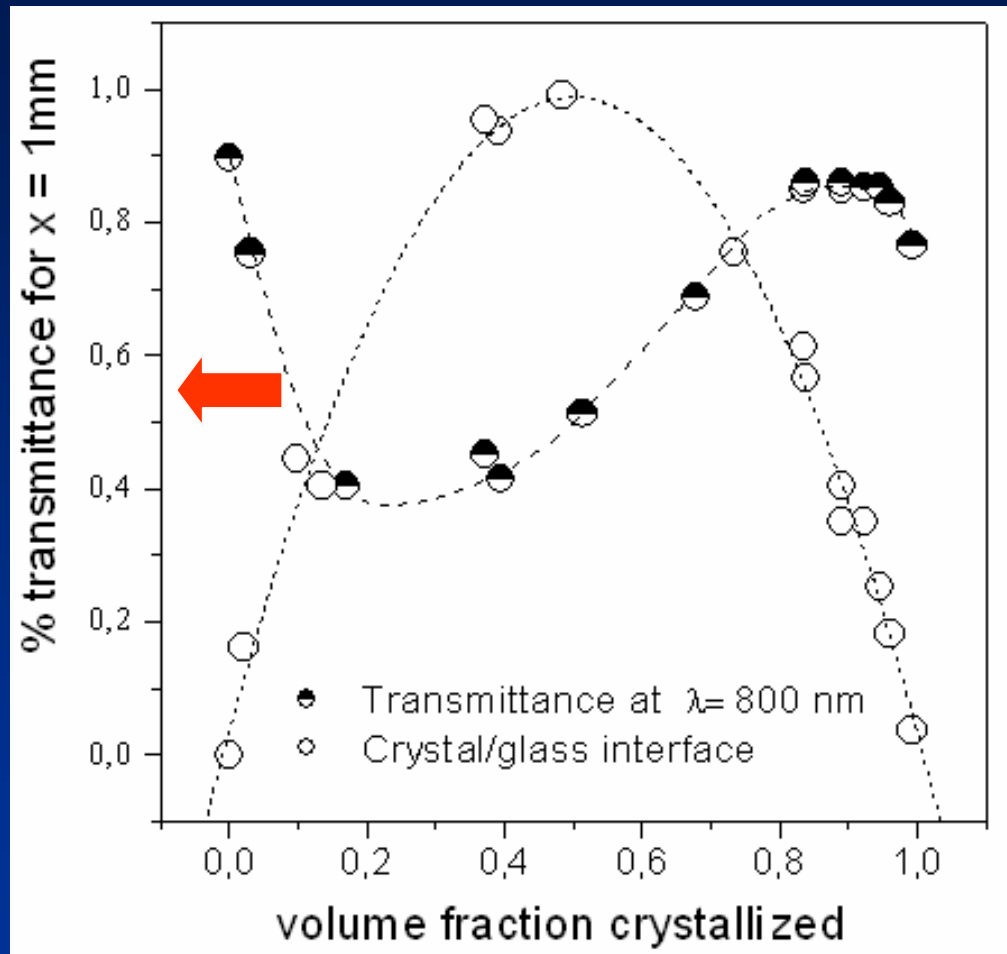
Affects P_2

Importance of thermal history

TRANSMITTANCE

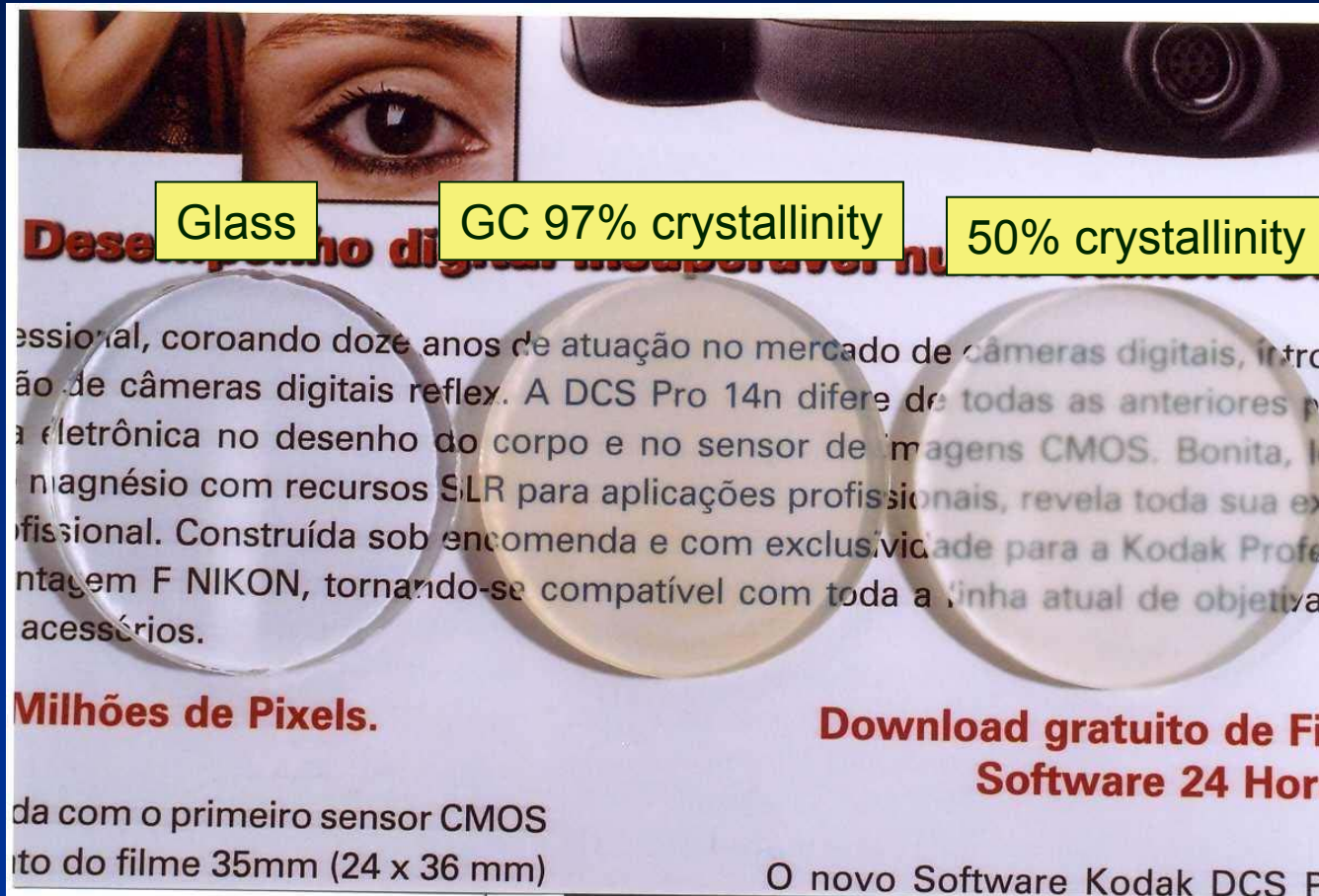
Degree of crystallinity

glass V8, cubic crystals (3-5 μm)

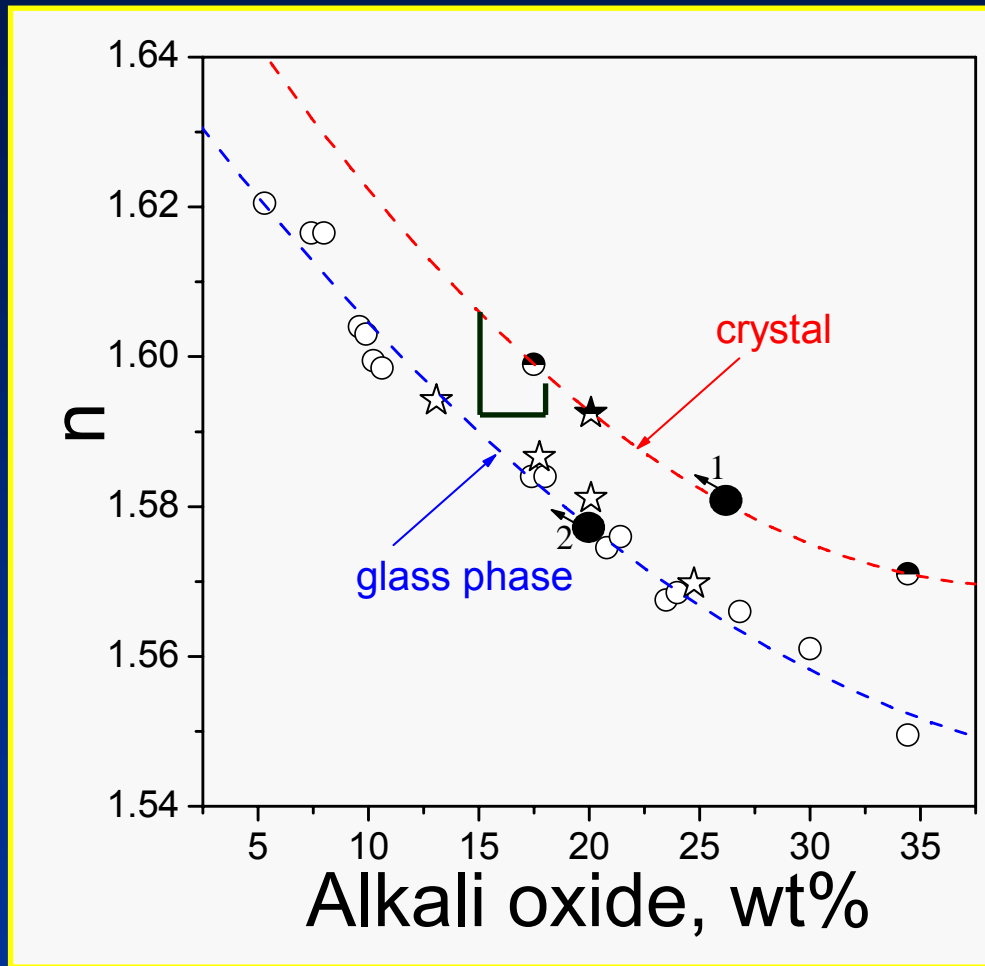


Glass V8 & T6, maximum transmission for ~ 95-97% OM crystallinity

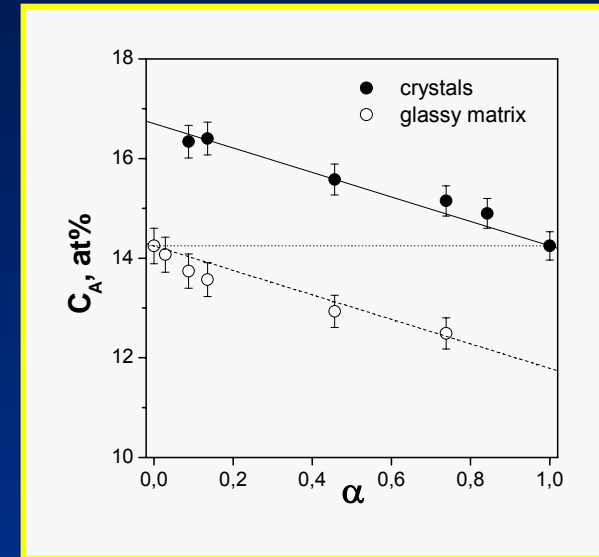
The beasts! Transparency of 4 mm thick specimens



DISCUSSION



EDS measurements



alkali content in
crystals

30% > glassy matrix

DISCUSSION

High crystallized 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**

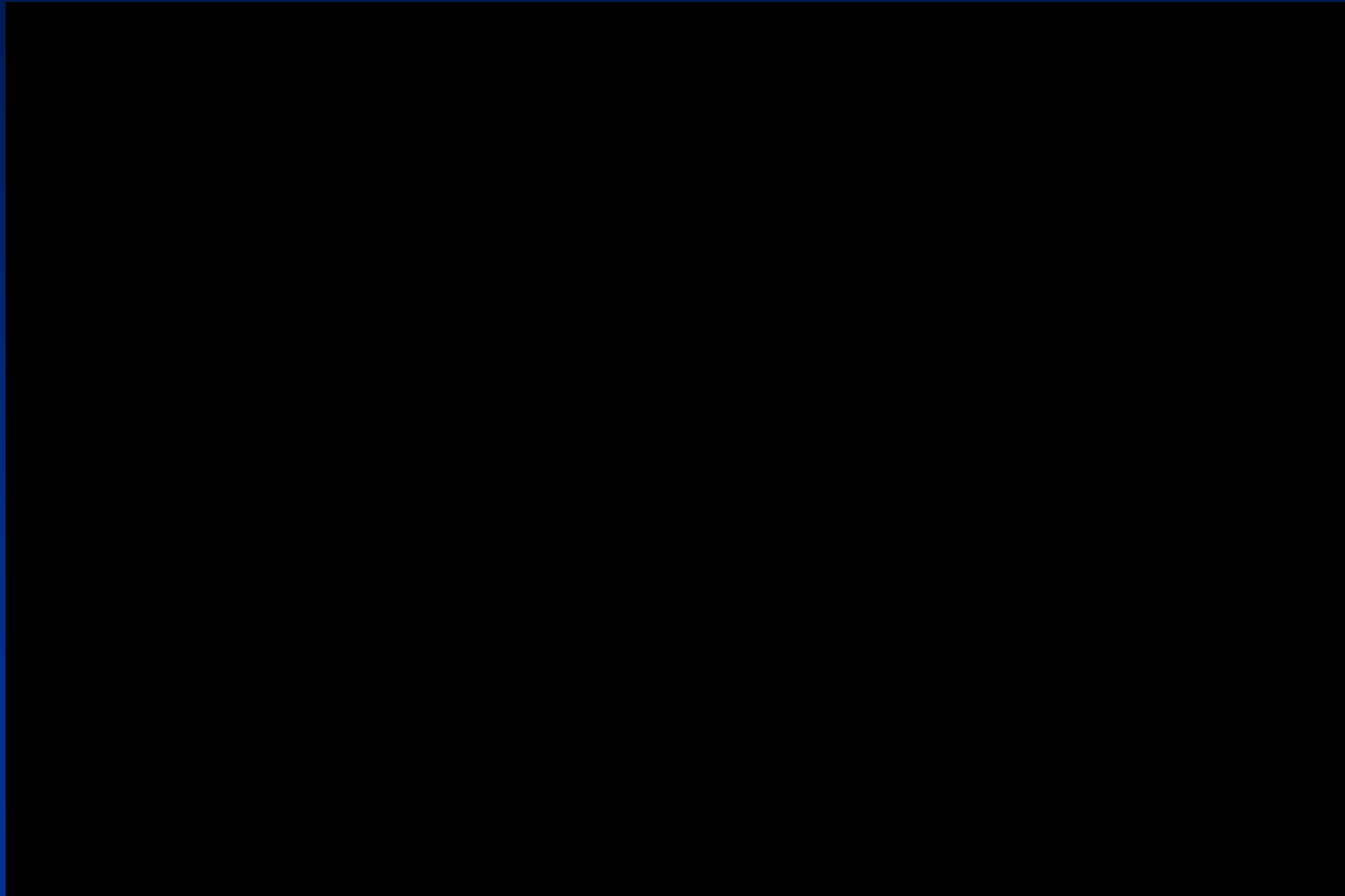


**Main reasons for improved
transparency in these new TGC**

- Mechanical behaviour of
HCHTGC

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

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



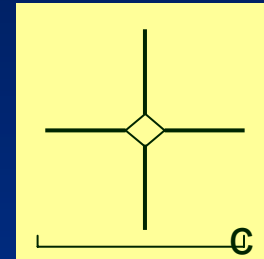
■ Don't try this
experiment in your
lab!

K_{IC} versus volume fraction crystallized

Average grain size
from 3 to 6 um

Anstis

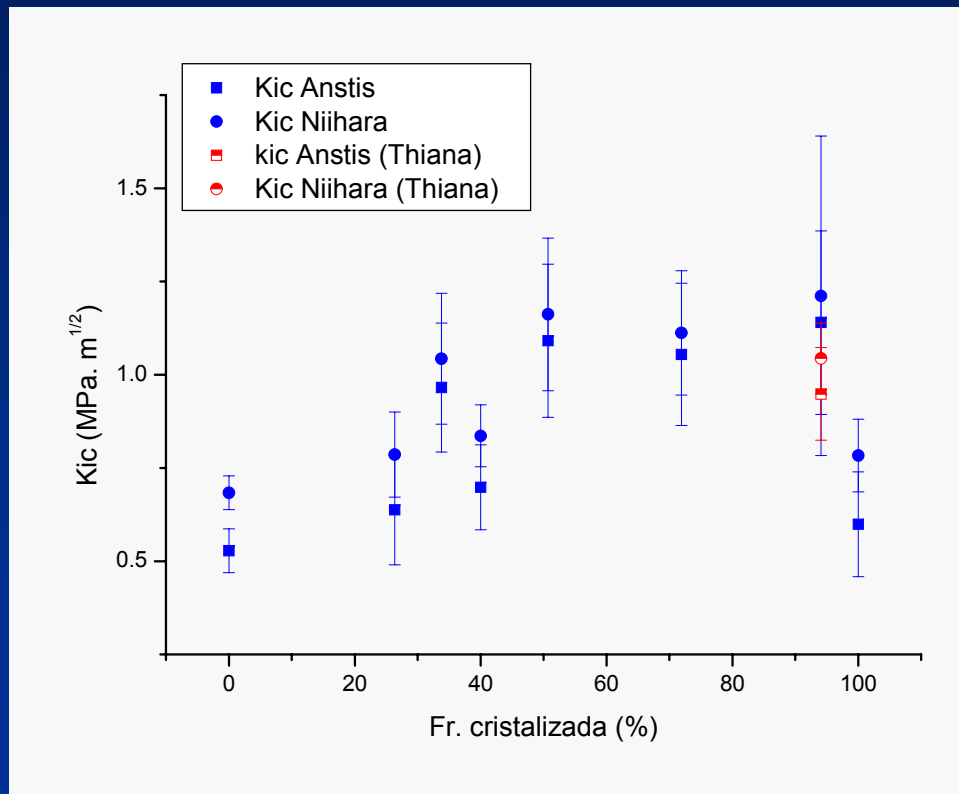
$$K_{IC} = 0.016 \left(\frac{E}{H} \right)^{\frac{1}{2}} \frac{F}{c^{\frac{3}{2}}}$$



Nihara

$$k_{IC} = 0.03 \left(\frac{l}{a} \right)^{\frac{1}{2}} \left(\frac{H}{E\phi} \right)^{\frac{2}{5}} \left(\frac{H\sqrt{a}}{\phi} \right)$$

$\phi \sim 3$,
 a, l, c [um]



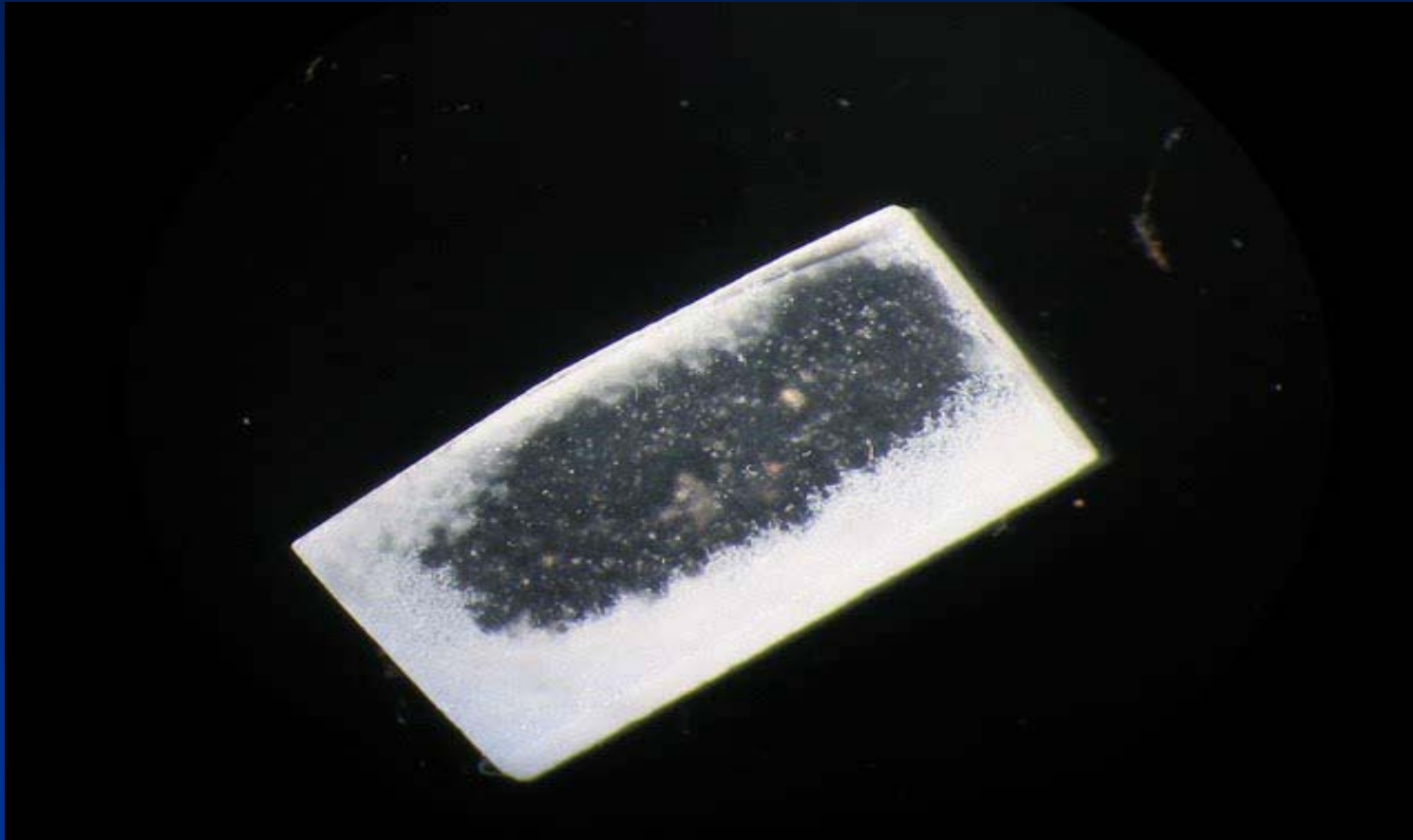
E_{glass}
71 GPa

$E_{\text{cr}} \sim 105$

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

SPONTANEOUS CRACKING for > 97% crystallinity!

accelerated 300X

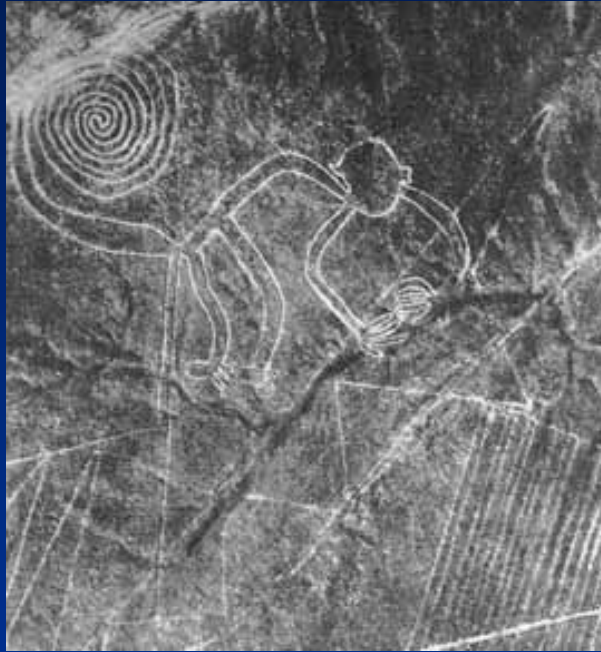


CONCLUSIONS

New
type of TGC 

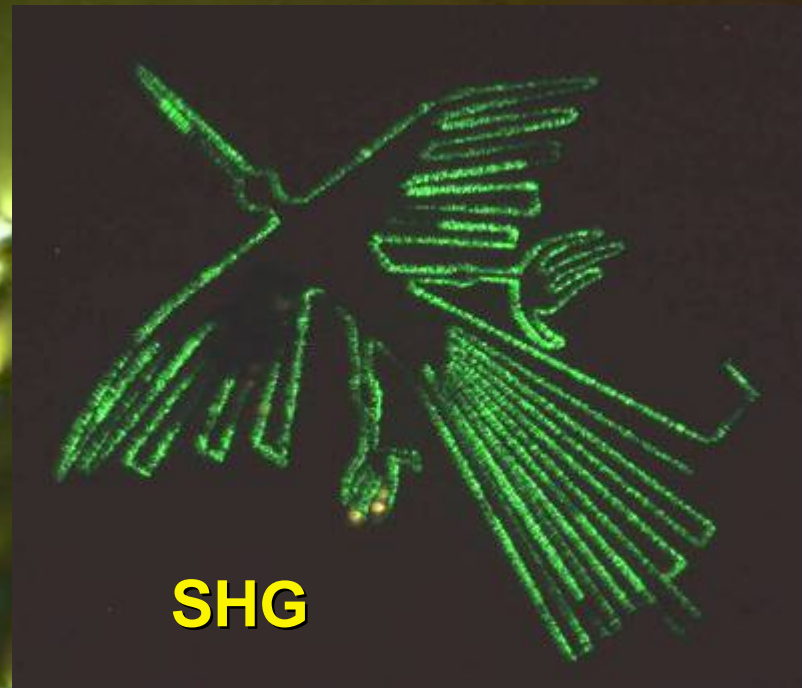
- highly transparent in the visible ~ 90% for 1mm
- nm to μm grain size
- up to 97% crystallized volume fraction
- chemical durability OK
- good mechanical properties, which can probably be much improved by ion-exchange.
- can be drawn into fibers
- luminescence ? doping with Cr and RE ions should be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

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



$\text{Sm}_2\text{O}_3\text{-Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ glass

$\text{Sm}_x\text{Bi}_{1-x}\text{BO}_3$ crystal



SHG

Crystals

Bird in Nazca, Peru

Courtesy of
T. Komatsu

300 μm

VITREOUS MATERIALS LAB, UFSCar, São Carlos BRAZIL



Thank you!

