III. Optical and mechanical properties of transparent glass-ceramics

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Optical and mechanical properties of mature and new transparent glass - ceramics

Edgar D. Zanotto

Federal University of São Carlos, Brazil

I IMI Meeting, State College, June 2005
OUTLINE

- Introduction to glass-ceramics
- Brief literature review on TGC
- Potential applications of TGC
- Conditions for transparency
- Mature TGC – nanocrystals
- **New TGC:**
  - 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
INTRODUCTION

GLASS-CERAMICS

- null porosity
- controlled volume crystallization
- null porosity
- designed microstructures: size & shape & uniform grain size, % crystallinity, etc.
- reproducible properties
  - high thermal and chemical stability
  - higher toughness than glasses
  - optical transparency

Interesting electrical properties

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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 generation;
- Substrates for LCD devices; optical amplifiers for up-conversion;
- 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

BEALL, G.H.; DUKE, D.A. TRANSPARENT GLASS-CERAMICS

Recent articles in the next slide
LITERATURE REVIEW (TGC in the 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

Derwent II
72 patents

Corning
Schott
Nippon
Others

30 years

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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)
Light attenuation

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

\[ R = \left( \frac{n-1}{n+1} \right)^2 \]
Basic requirements

- Transparent glass-ceramics
- Crystal size $\ll$ Wavelength of light
- 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
NEW
TRANSPARENT GC
(yet on the development stage)

![Graph and images showing properties of materials](image)

- **a, b**: no dopants;
- **c**: 5wt% Nd$_2$O$_3$;
- **d**: 5wt% Eu$_2$O$_3$;
- **e**: 5wt% Er$_2$O$_3$.

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.

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High alumina glasses and GC

Hardness against Al$_2$O$_3$ content. High-alumina glasses and glass-ceramics surpass other oxides: BeO, MgO, Y$_2$O$_3$, ZrO$_2$, TiO$_2$, Y$_3$Al$_5$O$_{12}$, Corning 9606 and 9608 GC, and are comparable to pure a-Al$_2$O$_3$ and b-Si$_3$N$_4$.

These compositions were also crystallized directly from the melt during slow cooling.
IR transmitting chalco-sulfide glass-ceramics

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


Lab. glasses and ceramics, University of Rennes, France
Typical microstructure of IR glass-ceramics

100nm CsCl crystals

Zhang et. al.

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IR transmission versus crystallinity

Zhang et. al.

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Night vision
Resistance to fracture propagation

Zhang et. al.

GC

Glass

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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
YAG-GC from glass-microstructure

As-made Cerammed

SEM

XRD

YAG

60% Crystalinity (wt%)

S. Tanabe et al.

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Moderate transmission of blue
Yellow fluorescence

Transmission $t = 0.5\text{mm}$

Emission

White light

Transmission.

Emission $(540\text{nm})$

Excitation $(460\text{nm})$

Ce:YAG G.C.

a) Ce:YAG GC

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

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# Solid-State Lighting (future)

## Promise of LEDs for illumination

<table>
<thead>
<tr>
<th>Light Source</th>
<th>Efficiency</th>
<th>Life</th>
</tr>
</thead>
<tbody>
<tr>
<td>Incandescent Light Bulb</td>
<td>16 lm/W</td>
<td>1000h</td>
</tr>
<tr>
<td>Fluorescent Lamp</td>
<td>80 lm/W</td>
<td>10,000h</td>
</tr>
<tr>
<td>Today’s white LED</td>
<td>60 lm/W</td>
<td>20,000h</td>
</tr>
<tr>
<td>Future white LED</td>
<td>200 lm/W</td>
<td>100,000h</td>
</tr>
</tbody>
</table>

*Efficiently bright, broad spectrum, long-lifetime…*

S. Tanabe et al.
Laser crystallization in Nagaoka

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

Department of Chemistry
Nagaoka University of Technology
Japan

Laser crystallization in glass

Rare-earth (Sm or Dy) atom heat processing

1. CW Nd:YAG laser irradiation to Sm2O3 or Dy2O3 containing glasses
2. Absorption and non-radiative relaxation
   Irradiated region is heated ➔ Crystallization

Writing of nonlinear optical/ferroelectric crystal dots and lines

- Sm2O3-BaO-B2O3 ➔ β-BaB2O4
- Sm2O3-Bi2O3-B2O3 ➔ SmxBi1-xBO3
- Sm2O3-MoO3-B2O3 ➔ β’-Sm2(MoO4)3
- Sm2O3-K2O-P2O5 ➔ KSm(PO3)4

Sm2O3-Bi2O3-B2O3 glass
SmxBi1-xBO3 crystal

Power: 0.66W
Scanning speed: 10μm/s

20,000 J/cm²
10Sm$_2$O$_3$.35Bi$_2$O$_3$.55B$_2$O$_3$ glass

$T_g=474^\circ C$, $T_x=574^\circ C$

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

Crystal

Temp. $>> T_x$

Temp. $< T_x$

Refractive index change

---


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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 - 45B₂O₃ - 15 TiO₂ (BBT)

Microstructures from two crystallization processes

BBT glass after irradiation with CO₂ laser ($\lambda = 10.6 \mu m$) 4 min, 40 W/cm². $= 10,000 \text{ J/cm}^2$

Glass at 300°C ($T_g = 580 \text{ °C}$)

BBT GC in resistive furnace at 620°C.

Mastelaro et. al.
Surface crystallization of BBT glass

It is possible to produce polycrystalline lines.

Details; crystals within the line and diffraction pattern

Mastelaro et. al.
SHG in partially crystallized BBT glass

Second harmonic generation

Laser beam
Nd:YAG (λ = 1064 nm)

Mastelaro et. al.
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$_2$O, ZnO, Al$_2$O$_3$, K$_2$O
  - **Minor:** F, Br
  - **Dopants (~100 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

UV excitation

Valence change

Photoionization

Electron trapping

Latent image

Silver atoms diffusion

Growth of Silver nanocrystal

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

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

Creol’s PTRG
Hologram
Leon Glebov et. al.

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LARGE GRAIN, HIGHLY CRYSTALLINE, HIGHLY TRANSPARENT GC

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

Simultaneous compositional variation of solid solution crystals and glassy matrix decreases $\Delta n$

New type of transparent glass-ceramic

Small or large grain size
High crystallized volume fraction
OPTICAL PROPERTIES

Transmittance measured for different sample thicknesses

Estimated parameters ($P_1$ and $P_2$):

\[ \frac{I}{I_0} = P_1 \exp(-P_2x) \]

\[ P_1 = (1-R)^2 \]

\[ P_2 = (\beta+S) \]

Crystal morphology

Grain size

Degree of crystallinity OM

Transmission Spectra

200 nm – 1100 nm

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

Their morphology can vary from \textit{J, spherical} to \textit{V8, cubic}
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

Morphology
glass J, spherical crystals, ~42% crystallized

The graph shows the transmittance for different wavelengths ($\lambda$) and grain sizes. The transmittance for a 1 mm thickness is plotted against the wavelength. The graph includes two lines, one for 7.5 $\mu$m grain size and another for 47 $\mu$m grain size. The $I(\lambda)$ dependence and the importance of thermal history are indicated by arrows. Crystal size affects $P_2$. Grain size also plays a role in the transmittance.

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glass V8, cubic crystals (3-5 μm)

Degree of crystallinity

Glass V8 & T6, maximum transmission for ~ 95-97% OM crystallinity
The beasts! Transparency of 4 mm thick specimens

- Glass
- GC 97% crystallinity
- 50% crystallinity
DISCUSSION

Alkali content in crystals

EDS measurements

30% > glassy matrix
DISCUSSION

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

High crystallized vol. fraction

- reduced crystal / glass interface

- refractive indexes of crystal and glass verge

- main reasons for improved transparency of these new TGC

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Mechanical behaviour of HCHT-GC

A new, specially designed, method of impact testing!
Don’t try this in your labs!
Kic versus volume fraction crystallized

Average grain size from 2 to 6 um

$E_{\text{glass}} = 71 \text{ GPa}$

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

$E_{cr} \sim 105$

$\phi \sim 3$, $a,l,c \ [\text{um}]$
Why do the transparency and impact strength drop significantly when crystallinity > 97%?
SPONTANEOUS CRACKING for > 97% crystallinity!

accelerated 300X
CONCLUSIONS

New type of TGC

- highly transparent in the visible ~ 90% for 1mm
- nm to \( \mu \)m grain size
- up to 97% crystallized volume fraction
- good mechanical properties, which can probably be much improved by ion-exchange.
- good chemical durability
- can be drawn into fibers
- luminescence ? doping with TM and RE ions should be tested...
On the origin of mysterious biomorphs and geoglyphs in Nazca, Peru, 200 B.C.
Sm$_2$O$_3$-Bi$_2$O$_3$-B$_2$O$_3$ glass  
Sm$_x$Bi$_{1-x}$BO$_3$ crystal

Bird in Nazca, Peru

SHG

Courtesy of T. Komatsu

300 μm