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
  - IR transmitting CG
  - Ce: YAG GC for lighting
  - Laser crystallized GC
  - PTR GC
  - LGHC GC
- Surprise....
- Conclusions
INTRODUCTION

null porosity

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

GLASS-CERAMICS

reproducible properties

high thermal and chemical stability

higher toughness than glasses

Interesting electrical properties

optical transparency

Vitreous Materials Lab – www.lamav.ufscar.br
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 gyrosopes; solar collectors; printed optical circuits; etc.
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

Vitreous Materials Lab – www.lamav.ufscar.br
Crystalline phases in TGC

- B–quartz ss
- B-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)
Light attenuation

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

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

atomic absorption (\(\beta\)) + surface reflection (R)
scattering (S)

Reflection losses (%)

0 2 4 6 8 10 12

1 1.2 1.4 1.6 1.8 2

Vitreous Materials Lab – www.lamav.ufscar.br
Conditions for transparency

Transparent glass-ceramics

crystal size $<<$ wavelength of light

Basic requirements

low birefringence

$n_{\text{glass}} \approx n_{\text{crystal}}$
Examples of commercially mature TGC
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)

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

**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.

50-90% Al$_2$O$_3$

2 mm tick

IR transparent
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 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.

Vitreous Materials Lab – www.lamav.ufscar.br
IR transmission versus crystallinity

Zhang et. al.

Vitreous Materials Lab – www.lamav.ufscar.br
Night vision
Resistance to fracture propagation

Zhang et. al.

GC

Glass

10 µm

Vitreous Materials Lab – www.lamav.ufscar.br
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

1cm

XRD

YAG

intensity / cps

60% Crystalinity (wt%)

S. Tanabe et al.

Vitreous Materials Lab – www.lamav.ufscar.br
Moderate transmission of blue
Yellow fluorescence

Transmission $t = 0.5\text{mm}$

Emission

White light emission from Ce:YAG G.C.

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

Vitreous Materials Lab – www.lamav.ufscar.br
Solid-State Lighting (future)

Promise of LEDs for illumination

<table>
<thead>
<tr>
<th></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 Sm$_2$O$_3$ or Dy$_2$O$_3$ containing glasses
2. Absorption and non-radiative relaxation
   Irradiated region is heated $\rightarrow$ Crystallization

Writing of nonlinear optical/ferroelectric crystal dots and lines

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

$\text{Sm}_2\text{O}_3$-$\text{Bi}_2\text{O}_3$-$\text{B}_2\text{O}_3$ glass
$\text{Sm}_{x}\text{Bi}_{1-x}\text{BO}_3$ crystal

Power: 0.66 W
Scanning speed: 10 $\mu$m/s

20,000 J/cm$^2$

Polarization optical microscope

Vitreous Materials Lab – www.lamav.ufscar.br
10Sm$_2$O$_3$.35Bi$_2$O$_3$.55B$_2$O$_3$ glass

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

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

crystal

Temp. >> $T_x$

Temp. < $T_x$

Refractive index change


Vitreous Materials Lab – www.lamav.ufscar.br
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$_2$O$_3$ - 15 TiO$_2$ (BBT)

Microstructures from two crystallization processes

BBT glass after irradiation with CO$_2$ laser ($\lambda = 10.6 \ \mu$m) 4 min, 40 W/cm$^2$.

= 10,000 J/cm$^2$

Glass at 300$^\circ$C ($T_g = 580$ $^\circ$C)

BBT GC in resistive furnace at 620$^\circ$C.

Mastelaro et. al.

Vitreous Materials Lab – www.lamav.ufscar.br
Surface crystallization of BBT glass

It is possible to produce policrystalline lines.

Details; crystals within the line and diffraction pattern

Mastelaro et. al.
SHG in partially crystallized BBT glass

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

Second harmonic generation

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: SiO₂, Na₂O, ZnO, Al₂O₃, K₂O
- 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

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.

Vitreous Materials Lab – www.lamav.ufscar.br
LARGE GRAIN, HIGHLY CRYSTALLINE, HIGHLY TRANSPARENT GC

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

Vitreous Materials Lab – www.lamav.ufscar.br
OPTICAL PROPERTIES

Transmission Spectra
200 nm – 1100 nm

Crystal morphology
Grain size
Degree of crystallinity OM

Transmittance measured for different sample thicknesses

Estimated parameters (P₁ and P₂):

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

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

\[
P_2 = (\beta+S)
\]
The crystals are solid solutions: $TA_{4+2x}AE_{4-x}\{GF_6O_{18}\}$ ($0 \leq x \leq 1$)

They can be spherical to cubic.

$T =$ trace element
$A =$ alkali
$AE =$ alkaline earth
$GF =$ Si, P, B
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
glass J, spherical crystals, ~42% crystallized

$\lambda$ dependence

Grain size

$I(\lambda)$ dependence

Crystal size

Affects $P_2$

Importance of thermal history
glass V8, cubic crystals (3-5 µm)

Degree of crystallinity

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

Vitreous Materials Lab – www.lamav.ufscar.br
The beasts! Transparency of 4 mm thick specimens
DISCUSSION

EDS measurements

alkali content in crystals

30% > glassy matrix
DISCUSSION

High crystallized vol. fraction

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

reduced crystal / glass interface

refractive indexes of crystal and glass verge

main reasons for improved transparency of these new TGC

Vitreous Materials Lab – www.lamav.ufscar.br
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

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

$E_{cr} \sim 105$

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

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

accelerated 300X
CONCLUSIONS

- highly transparent in the visible ~ 90% for 1mm
- nm to µm 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...

Vitreous Materials Lab – www.lamav.ufscar.br
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

Crystals

Courtesy of T. Komatsu