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

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Transparent glass - ceramics

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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:**

- 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

GLASS-CERAMICS

- Controlled volume crystallization
- Designed microstructures: size & shape, uniform grain size, % crystallinity, etc.
- Reproducible properties
- Optical transparency
- Null porosity
- High thermal and chemical stability
- Tougher than glasses
- Interesting electrical properties

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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-converter;
- 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
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 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

30 years

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Crystalline phases in TGC

- B–quartz ss
- B-eucryptite
- Mullite
- Spinel
- Willemite
- Ghanite
- Forsterite
- \(\beta\)-BBO
- \(\text{LiNbO}_3\)
- \(\text{NaNbO}_3\)
- \(\text{PbF}_2\)
- \(\text{LaF}_3\)
- ZnO
- Etc.

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

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 (%)

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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
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)

**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.
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 $\alpha$-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


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

100nm CsCl crystals

Zhang et. al.
IR transmission \textit{versus} crystallinity

Zhang et. al.
Night vision
Resistance to fracture propagation

Zhang et. al.

GC

Glass
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

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# 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>1000$h$</td>
</tr>
<tr>
<td>Fluorescent Lamp</td>
<td>80 $lm / W$</td>
<td>10,000$h$</td>
</tr>
<tr>
<td>Today’s white LED</td>
<td>60 $lm / W$</td>
<td>20,000$h$</td>
</tr>
<tr>
<td>Future white LED</td>
<td>200 $lm / W$</td>
<td>100,000$h$</td>
</tr>
</tbody>
</table>

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

S. Tanabe et al.
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

Excitation (460nm)

Ce:YAG GC

Emission (540nm)

a) Ce:YAG GC

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

White light

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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 (Samarium) 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  →  Crystallization

Writing of nonlinear optical/ferroelectric crystal dots and lines

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

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

Power: 0.66W  
Scanning speed: 10µm/s

Nagaoka

20,000 J/cm$^2$

Polarization optical microscope

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10Sm2O3·35Bi2O3·55B2O3 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 - 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.
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

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

Second harmonic generation

Mastelaro et. al.
PTR Glasses

Oxy fluor bromide glasses

- Composition
- Major: SiO$_2$, Na$_2$O, ZnO, Al$_2$O$_3$
- Minor: K$_2$O, F, Br
- Dopants (~200 ppm): Ag, Ce, Sb, Sn
- Impurities (< 2 ppm): transition metals

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

Feliz Aniversario
Vladimir

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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

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

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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

$I(\lambda)$ 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
The beasts! Transparency of 4 mm thick specimens

Glass
GC 97% crystallinity
50% crystallinity
DISCUSSION

EDS measurements

alkali content in crystals
30% > glassy matrix

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DISCUSSION

Main reasons for improved transparency in these new TGC

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

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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 μm

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

\[ E_{glass} = 71 \text{ GPa} \]

\[ E_{cr} \approx 105 \]

\[ kic = 0.035 \left( \frac{1}{a} \right)^{\frac{1}{2}} \left( \frac{H}{E\phi} \right)^{\frac{2}{5}} \left( \frac{H\sqrt{a}}{\phi} \right) \]

\[ \phi \approx 3, \quad a, l, c \ [\text{um}] \]

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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 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

300 μm
Thank you!