Crystallization of RE Ions Doped Transparent Glass Ceramics

Yuansheng Wang

Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences
1、General Crystallization Process

Crystallization may take place in solution or amorphous system

Crystallization includes two stages

<table>
<thead>
<tr>
<th>Component ions</th>
<th>Nucleation (Stage I)</th>
<th>Nucleus</th>
<th>Growth (Stage II)</th>
<th>Grains</th>
</tr>
</thead>
</table>

Nucleation rate < Nucleus growth rate

Less grain
Large size

Nucleation rate > Nucleus growth rate

More grain
Small size
Schematic illustration of nucleation + growth of crystal
Component ions distribute randomly in amorphous matrix
Component ions aggregate to form clusters
Some clusters grow to form ordered nucleus of critical size
Nucleus grow to form grain through diffusions of ions
Grains grow until component ions are exhausted

Further heating → Second grain growth (Ostwald Ripening)
Main factors affect grain purity

- adsorption
- occlusion
- inclusion
- mixed crystal solid solution
Examples of impurity

- **CuO**
- **PbSO₄**

Mixed phase:
- Different crystalline structure

Solid solution:
- Similar ionic radius, same crystalline structure
2、Crystallization of Glass Ceramics

Applications of Luminescent Materials

(Powder & Bulk)

LED

Fluorescent Lamp

Solid State Laser

Optical Fiber & Amplifier

Display
Novel luminescent bulk material:
Rare-earth Ions Doped Transparent Oxyfluoride Glass Ceramics

Combines both advantages from fluoride crystal and oxide glass

Crystal
+: excellent optical spectral properties
-: high cost, difficult growth to large size

Glass
+: low cost, easy fabrication in large size
-: worse optical spectral properties

Glass ceramic
Oxide glass matrix
Fluoride nanocrystals doped with active RE ions

Tranditional luminescent bulk materials
Material’s structure determines its performances

What is favorable microstructure for TGC?

To achieve:
High transparency + Efficient light emission

- Homogenous oxide glass matrix
- Mono-dispersed fluoride phase
- Spherical nanocrystals (< 20 nm)
- RE ions partitioned in crystal lattices
What we need?

RE ions doped transparent oxyfluoride glass ceramic: A composite material of low phonon energy fluoride nanocrystals incorporated with RE ions embedding among an oxide glassy matrix

Why fluoride crystal?

Fluoride phase has low phonon energy, which reduces the multi-phonon non-radiative de-excitation of RE ions, results in a high emission efficiency

Why oxide glass matrix?

Most oxide glasses exhibit high mechanical strength and chemical stability, suitable for practical industry applications

Why nanocrystals?

Much smaller size of the precipitated fluoride crystals than the wavelength of the visible and infrared light (or the matching of the refractive index between nano-crystals and glassy host) ensures the high transparency of glass ceramic
How to achieve desired microstructure: controlled nucleation and growth of nanocrystals from precursor glass

Key points:

- Appropriate composition of precursor glass (several components),
- Revealing crystallization kinetics (determine $E$, $n$),
- Setting crystallization (heating) temperature ($T_c$ around $T_p$),
- RE acting as nucleation agent (usually, not necessary)
Preparation of precursor glass

Chemicals fully mixed → Heated in platinum crucible at 1400°C → Completely molten

Precursor glass

Annealed to release stress → Poured into pre-heated copper mold and cooled down to room temperature
Crystallization Kinetics of Glass

Crystallization = Nucleation + Grain Growth

For the crystallization system with nucleation and growth processes following the Arrhenius rule

\[ x = 1 - \exp(-Kt)^n \]  \hspace{1cm} \text{JMA equ.}

\[ K = K_0 \exp\left(-\frac{E_a}{RT}\right) \]  \hspace{1cm} \text{Arrhenius equ.}

\( x \): crystallized volume fraction at time \( t \);
\( K \): a function of temperature \( T \), is related to the nucleation and growth rate;
\( R \): gas constant;
\( n \): Avrami exponent which reflects crystallization mechanism;
\( E_a \): apparent activation energy for crystallization;
Based on JMA and Arrhenius equations

Apparent activation energy $E_a$ and Avrami exponent $n$, two most important kinetic parameters describing crystallization mechanism, can be determined from non-isothermal DSC/DTA measurements using Chen’s or Ozawa’s equations.

Chen’s equation:

$$\frac{d \left[ \ln \left( T_p^2 / \alpha \right) \right]}{d \left( 1 / T_p \right)} = \frac{E_a}{R}$$

Ozawa’s equation:

$$\frac{d \ln \alpha}{d \left( 1 / T_p \right)} = -\frac{E_a}{R}$$

Ozawa’s equation:

$$\left. \frac{d \left\{ \ln \left[ -\ln \left( 1 - x \right) \right] \right\}}{d \ln \alpha} \right|_{T_x} = -n$$

$\alpha$: heating rate;
$T_p$: crystallization temperature at a given heating rate;
$x$: crystallized volume fraction at a fixed temperature $T_x$ with heating rate $\alpha$. 
Example illustrating the determination of $E_a$ and $n$ for crystallization in glass matrix

$r$ is the correlative coefficient of least-squares fitting
Various kinds of crystallization mechanisms

<table>
<thead>
<tr>
<th>(a) polymorphous crystallization, interface controlled growth</th>
<th>n value</th>
</tr>
</thead>
<tbody>
<tr>
<td>increasing nucleation rate</td>
<td>&gt; 4</td>
</tr>
<tr>
<td>constant nucleation rate</td>
<td>4</td>
</tr>
<tr>
<td>decreasing nucleation rate</td>
<td>3-4</td>
</tr>
<tr>
<td>zero nucleation rate</td>
<td>3</td>
</tr>
<tr>
<td>interfacial nucleation (saturated)</td>
<td>1</td>
</tr>
<tr>
<td>grain edge nucleation (saturated)</td>
<td>2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(b) diffusion controlled grain growth</th>
<th>n value</th>
</tr>
</thead>
<tbody>
<tr>
<td>increasing nucleation rate</td>
<td>&gt; 2.5</td>
</tr>
<tr>
<td>constant nucleation rate</td>
<td>2.5</td>
</tr>
<tr>
<td>decreasing nucleation rate</td>
<td>1.5-2.5</td>
</tr>
<tr>
<td>zero nucleation rate</td>
<td>1.5</td>
</tr>
<tr>
<td>growth from preexisted precursors</td>
<td>1-1.5</td>
</tr>
<tr>
<td>thickening of large plates</td>
<td>0.5</td>
</tr>
<tr>
<td>film growth</td>
<td>1</td>
</tr>
<tr>
<td>threads growth</td>
<td>2</td>
</tr>
</tbody>
</table>

(determined by $E_a$ value)
Several examples of crystallization for fluoride nanocrystals in glasses

CaF$_2$:Er contained GC

Er ions acted as nucleation agent to promote crystallization

Using Debby-Scherrer formula, mean sizes of CaF$_2$ crystals were evaluated to be 5, 9, 15 and 38 nm for b, c, d, and e samples
Crystallization mechanism of CaF$_2$

<table>
<thead>
<tr>
<th>Sample</th>
<th>T$_p$ (℃)</th>
<th>$E_a$ (kJ/mol)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Chen's method</td>
<td>Ozawa’s method</td>
</tr>
<tr>
<td>x=0.0</td>
<td>647</td>
<td>299</td>
<td>314</td>
</tr>
<tr>
<td>x=0.1</td>
<td>633</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=0.5</td>
<td>621</td>
<td>314</td>
<td>329</td>
</tr>
<tr>
<td>x=1.0</td>
<td>616</td>
<td></td>
<td></td>
</tr>
<tr>
<td>x=2.0</td>
<td>608</td>
<td>332</td>
<td>347</td>
</tr>
</tbody>
</table>

Crystallization was a diffusion-controlled growth from small dimensions with decreasing nucleation rate.

- This mechanism implies: local composition changes during crystallization, and crystal growth rate depends exponentially on heating temperature.
- Accordingly, controllable crystallization could be conducted mainly by adjusting heating temperature and (or) modifying composition of precursor glass.
Where were Er ions located?

EDS spectra with nano-sized probe from: (a) glass matrix, and (b) an individual nanocrystal, of 2 mol% Er doped glass ceramic

Er ions aggregated in CaF$_2$ nanocrystals (lattices and surfaces)
After Er-doping, CaF$_2$ crystal size reduced, while its number density increased.

Crystallization Temperature $T_p$ decreased with increasing of Er content $x$

Some of Er$^{3+}$ ions segregated on crystal surfaces which slightly enhanced the crystallization activation energy to retard the crystal growth by hindering the atomic diffusions.
(a) Upconversion emission, and (b) near-infrared emission spectra of glass ceramics under 980 nm excitation

**Crystallization induced**: Intensification of up-conversion emissions, Spark splitting of emission bands

Some of Er ions partitioned in CaF$_2$ crystalline lattices with low phonon energy
BaF$_2$:Er contained GC

**Diagram:**
- **500°C**

- **800°C**

**Graphs:**
- **Intensity (a.u) vs. Wavelength (nm)**
- **Lattice parameter (angstrom)**
- **2-theta (degree) vs. Intensity (a.u)**
- **Energy transitions:** $^2H_{11/2} \cdot ^4S_{3/2} \rightarrow ^4I_{15/2}$

**From glass matrix**

**From crystallite**

$\lambda_{exc}=378$
NaYF₄:Nd contained GC

- Kinetic studies reveal the crystallization mechanism being a diffusion-controlled growth of particles with decreasing nucleation rate.
- Nd³⁺ ions acted as nucleation agent and promoted NaYF₄ crystallization.
- Expansion of cubic NaYF₄ lattice with increasing of Nd³⁺ content indicates incorporation of Nd³⁺ into NaYF₄ lattice by substituting Y³⁺.

All samples were 620°C heated

(a) Nd-free; (b) 1% Nd; (c) 3% Nd
**YF₃:Nd contained GC**

Nd acted as nucleation agent for YF₃ crystallization.

Compared with standard pattern, diffraction peaks of YF₃ nanocrystals shift to the lower angle side.

EDX spectra with nano-sized probe taken from an individual nanocrystal (d) and from glass matrix (e).

Incorporation of Nd³⁺ with radius of 0.126nm into YF₃ by substituting Y³⁺ ions with radius of 0.116nm.
General nanocrystallization of LnF$_3$ (Ln = La–Lu,Y) in SiO$_2$–Al$_2$O$_3$–NaF–LnF$_3$ glasses

• These fluorides (from LaF$_3$ to LuF$_3$) exhibited dimorphism, i.e., the hexagonal structure for those from LaF$_3$ to GdF$_3$, and the orthorhombic one for those from TbF$_3$ to LuF$_3$ (including YF$_3$).

• For all the systems, doped RE ions partitioned into the LnF$_3$ nanocrystals.
PbF$_2$:Er contained GC

What were differences?

- PbF$_2$ crystallized during melt-quenching,
- Nanocrystals aggregated together,
- Congeries size increased with Er doping,
- Grains grown through Ostwald Ripening

(a) 0 mol% Er, (b) 1 mol% Er, (c) 2 mol% Er and (d) 4 mol% Er

500$^\circ$C heat treated

incorporation of small grains to a bigger one
Phase separation determined nucleation and crystallization

What were differences?

Yb$_2$O$_3$–Y$_2$O$_3$–SiO$_2$  GC

- Spherical phase
- Matrix phase
- Crystobalite

Temperature:
- 500 ºC
- 700 ºC
- 800 ºC
- 1000 ºC
- 1050 ºC
- 1150 ºC

- $\alpha$-Y$_2$Si$_2$O$_7$
Thanks for attention
Various glass ceramic samples

(a) SiO$_2$-$\text{Al}_2\text{O}_3$-$\text{Na}_2\text{O}$-$\text{LaF}_3$ ;   (b) SiO$_2$-$\text{Al}_2\text{O}_3$-$\text{Na}_2\text{O}$-$\text{LaF}_3$:Er ;
(c) SiO$_2$-$\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{NaF}$-$\text{CaF}_2$:Er ;   (d) SiO$_2$-$\text{Al}_2\text{O}_3$-$\text{CaO}$-$\text{NaF}$-$\text{CaF}_2$:Er/Yb
Mixed crystal or solid solution

**Homo type**
- Similar radius, same structure
  - \( \text{BaSO}_4 - \text{PbSO}_4 \)
  - \( \text{AgCl} - \text{AgBr} \)

**Hetero type**
- Different crystalline structure
  - \( \text{BaSO}_4 - \text{CuO} \)