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Crystallization of RE Ions Doped Transparent Glass Ceramics

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1、 General Crystallization Process

Crystallization may take place in solution or amorphous system

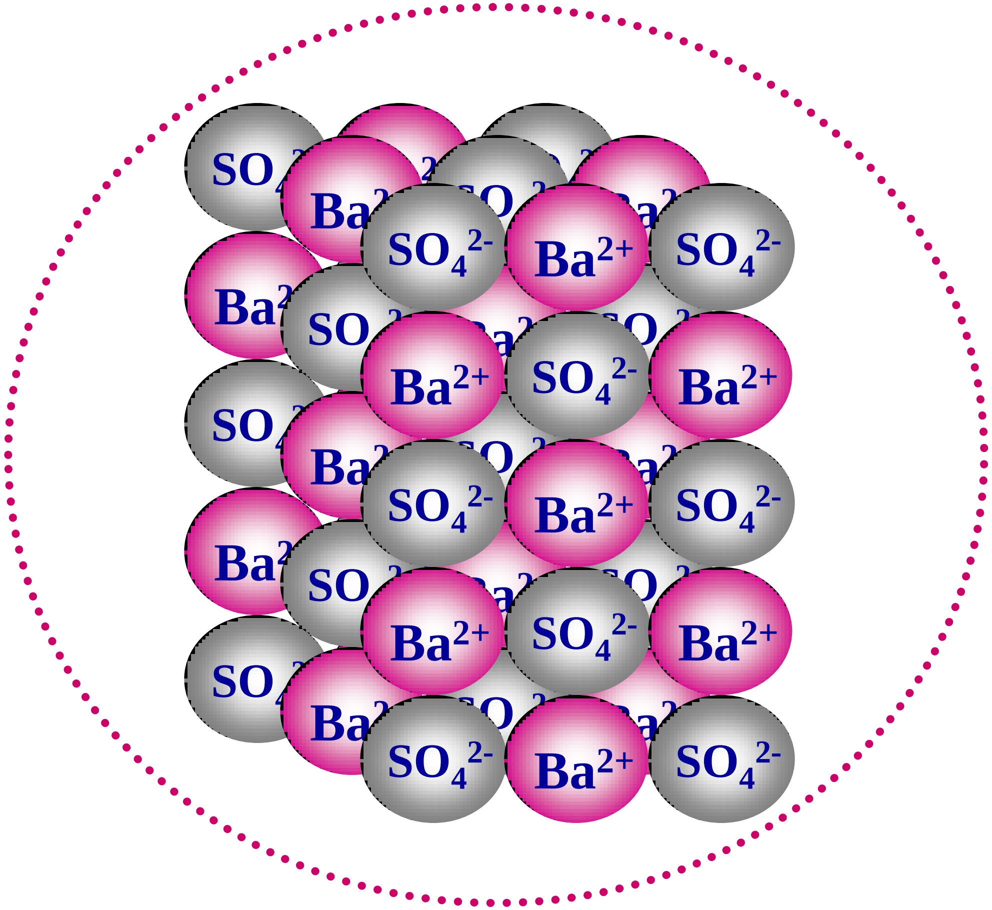
Crystallization includes two stages

Component ions —Nucleation (Stage I)→ **Nucleus** —Growth (Stage II)→ **Grains**

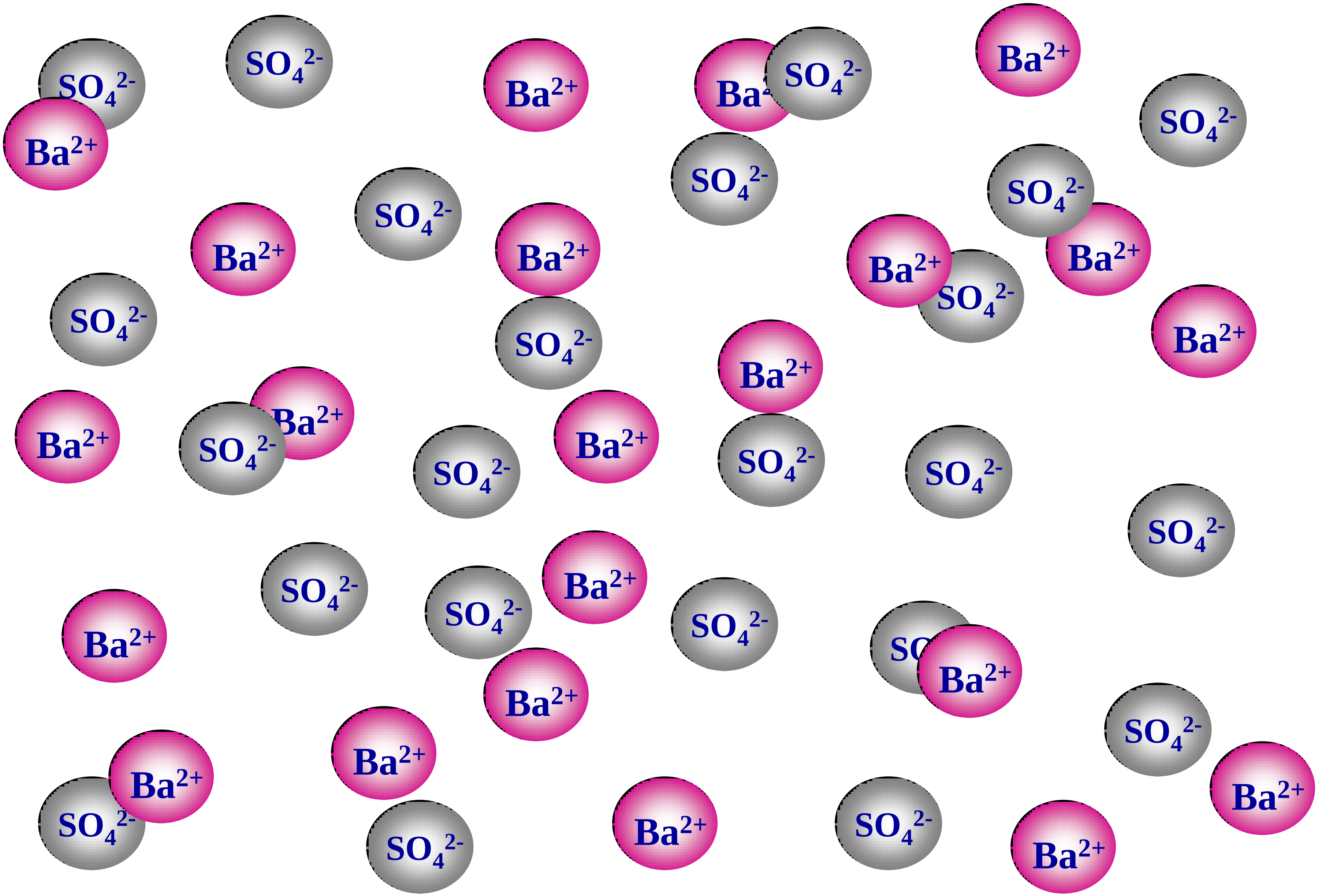
Nucleation rate < Nucleus growth rate ⇒ **Less grain, Large size**

Nucleation rate > Nucleus growth rate ⇒ **More grain, Small size**

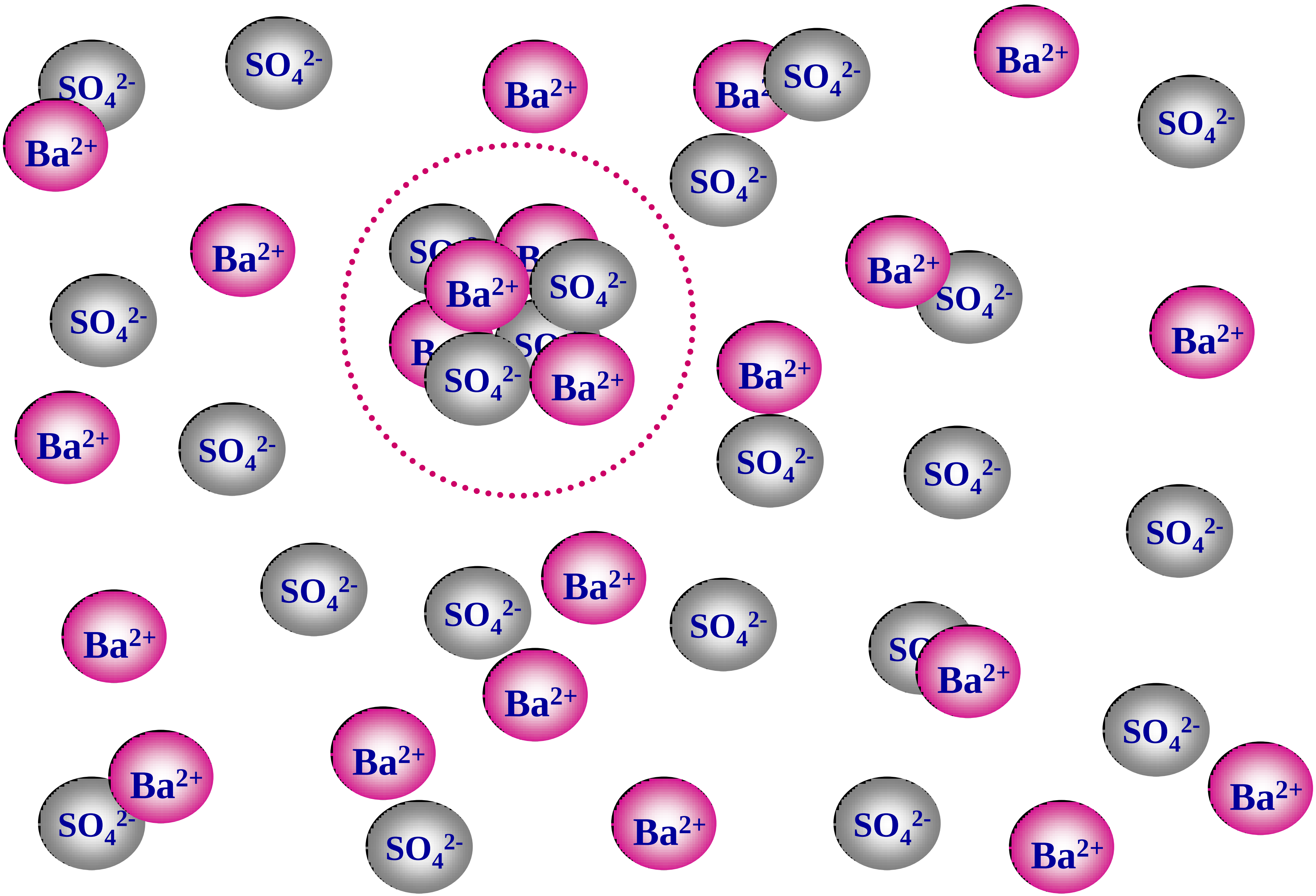
Schematic illustration of nucleation + growth of crystal



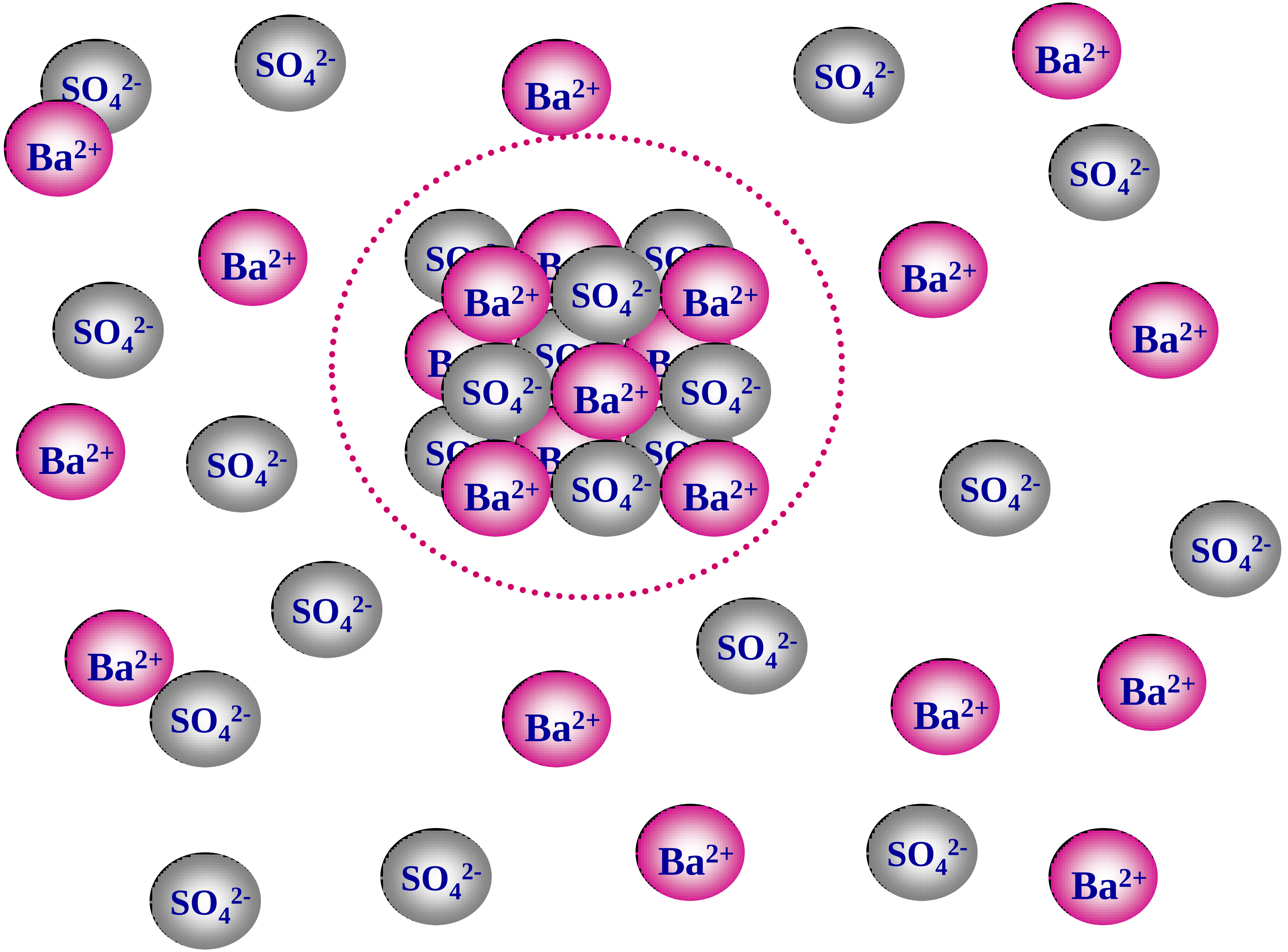
Component ions distribute randomly in amorphous matrix



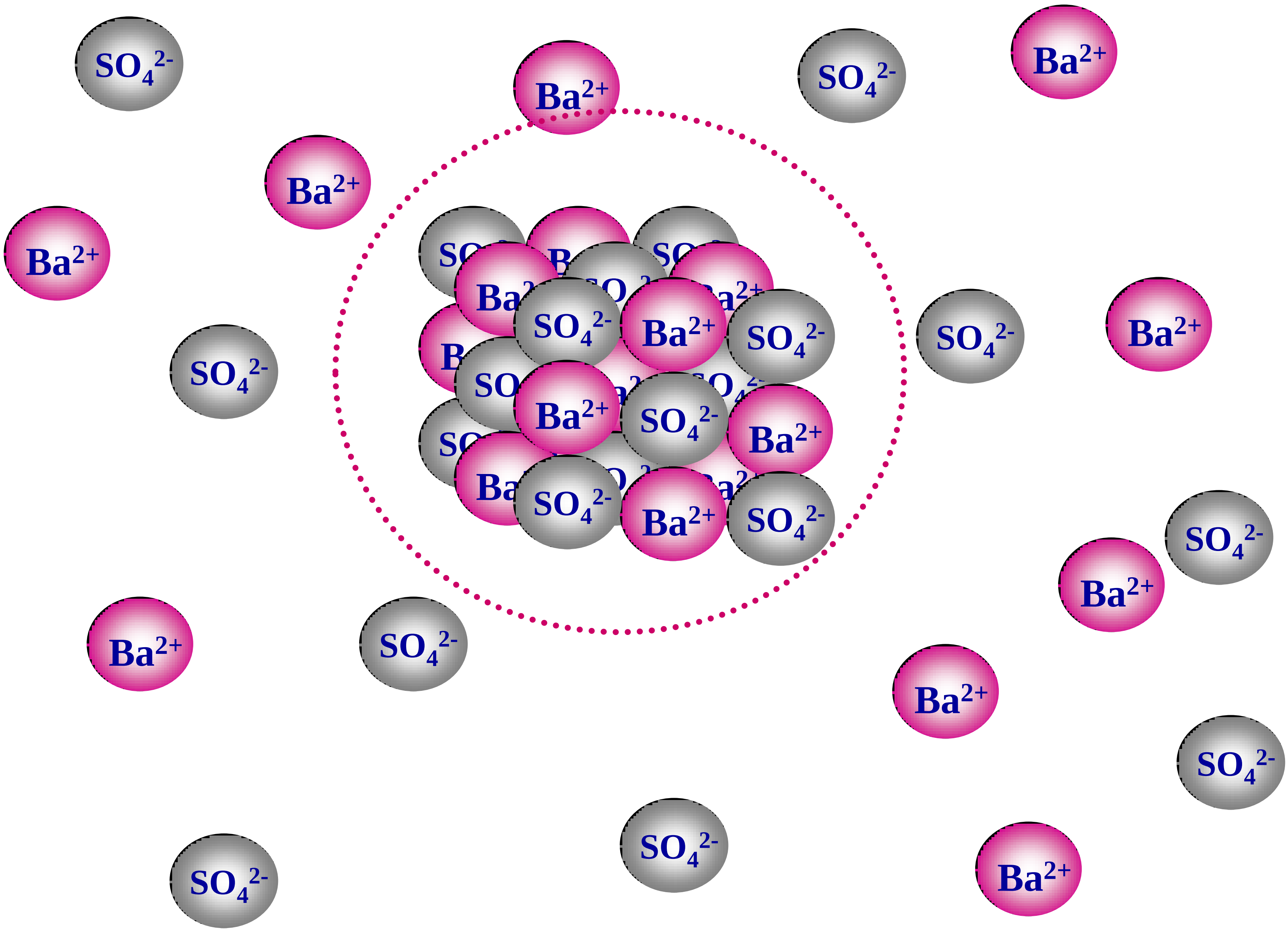
Component ions aggregate to form clusters



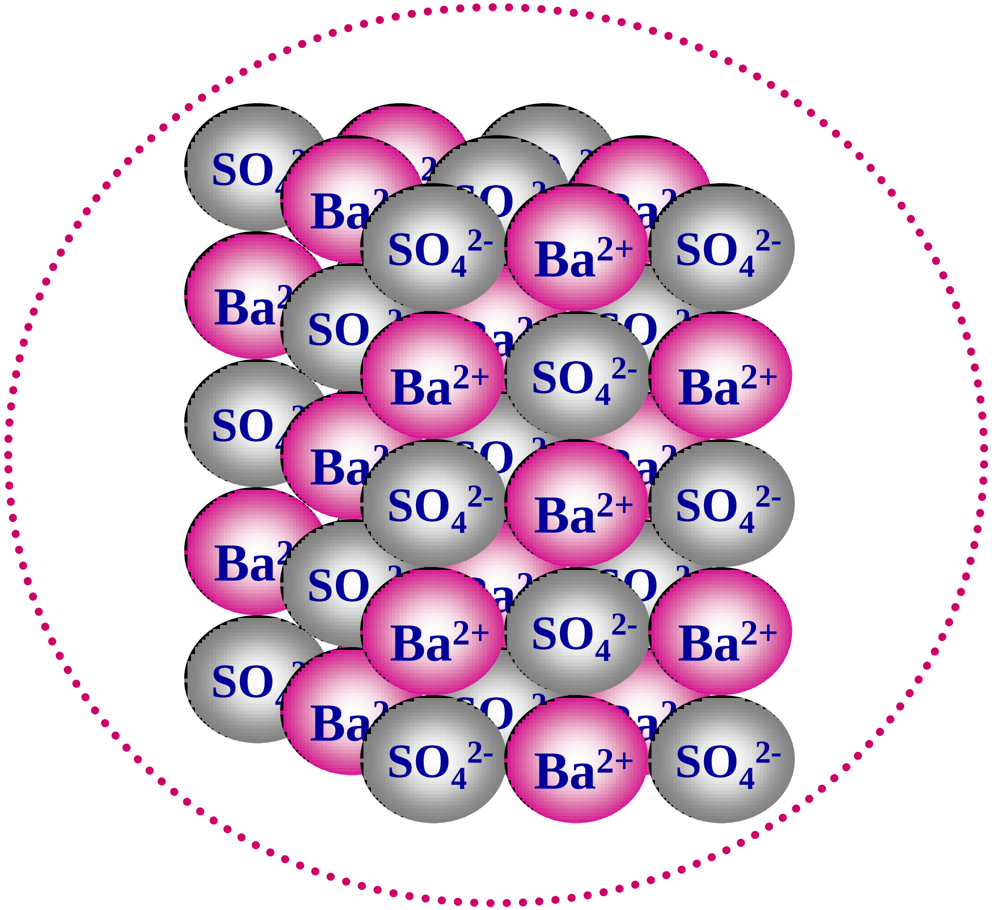
Some clusters grow to form ordered nucleus of critical size

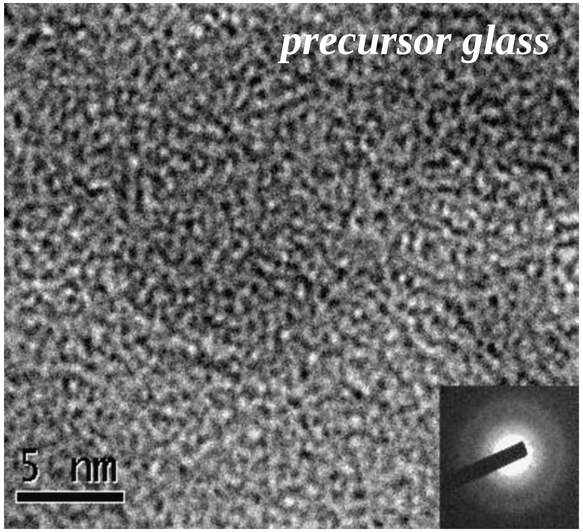


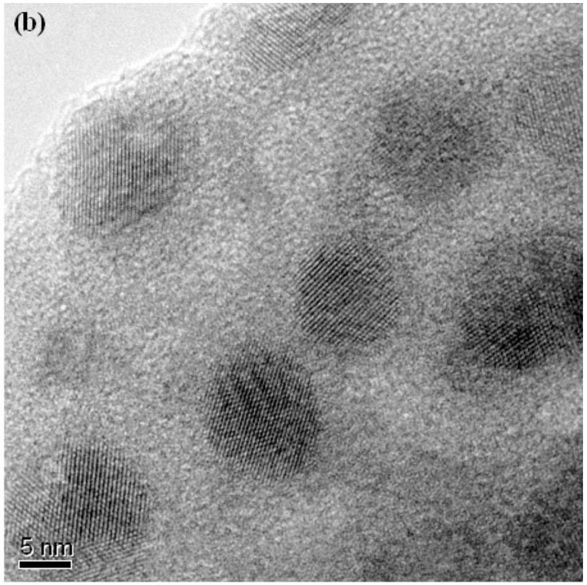
Nucleus grow to form grain through diffusions of ions



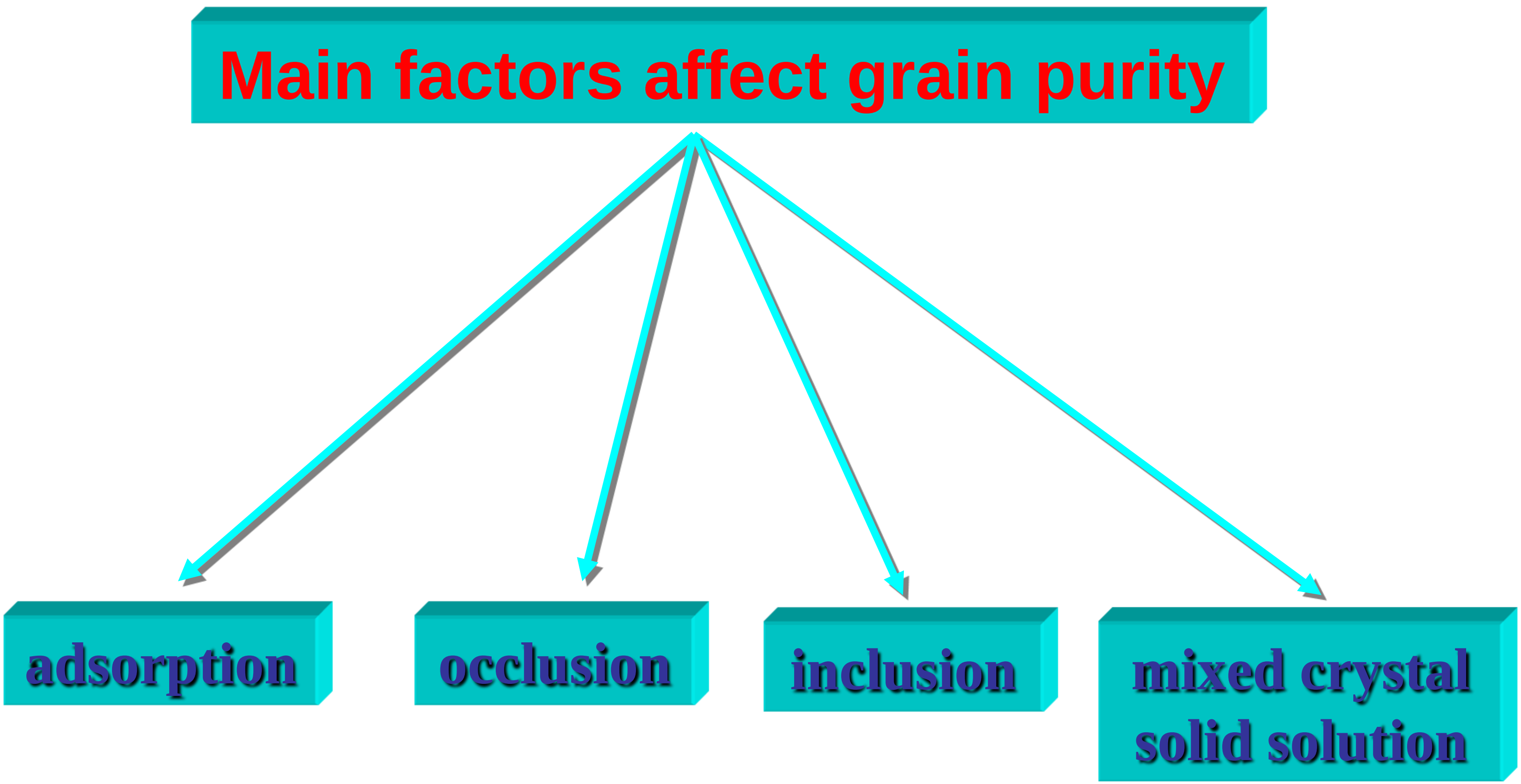
Grains grow until component ions are exhausted



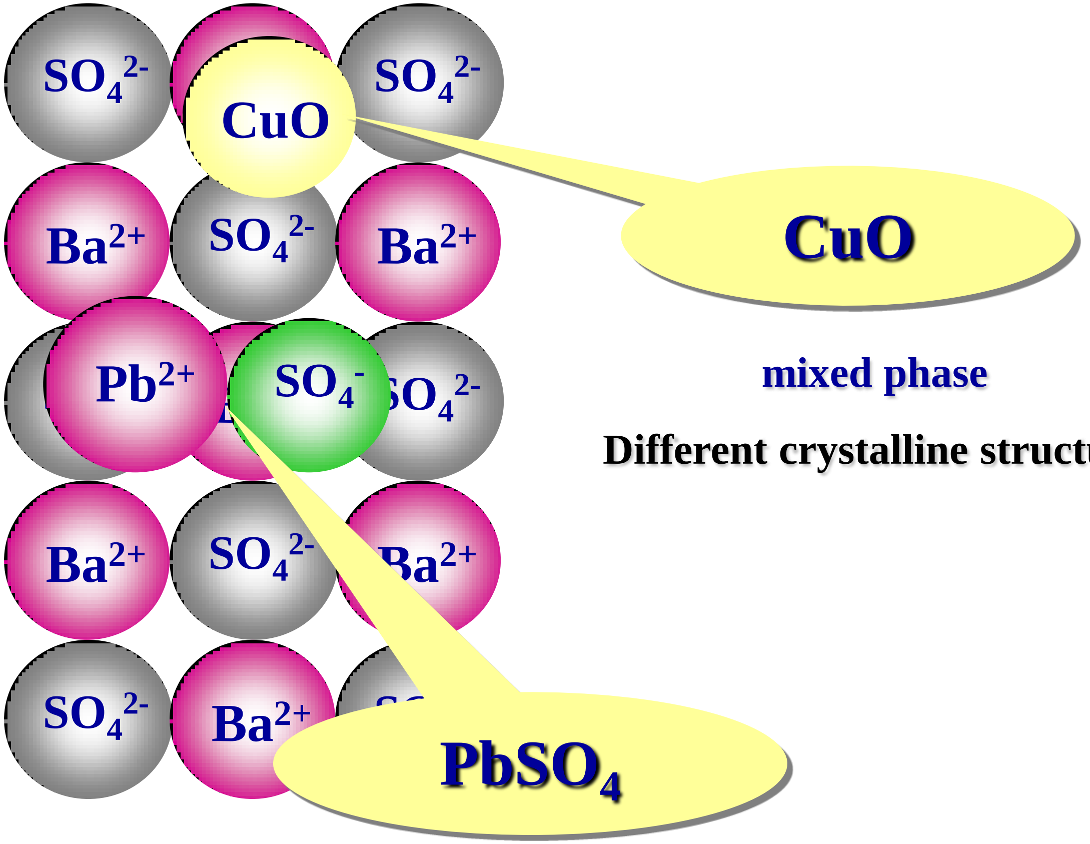




Further heating ⇨ Second grain growth (Ostwald Ripening)


Main factors affect grain purity
adsorption
occlusion
inclusion
mixed crystal
solid solution

Examples of impurity



mixed phase

Different crystalline structure

solid solution

Similar ionic radius, same crystalline structure

2、Crystallization of Glass Ceramics

Applications of Luminescent Materials (Powder & Bulk)

Display

LED

Fluorescent Lamp

Solid State Laser

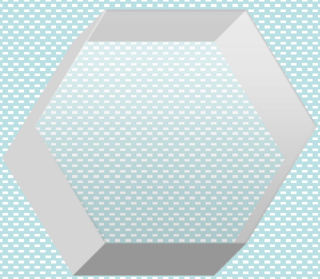
Optical Fiber & Amplifier

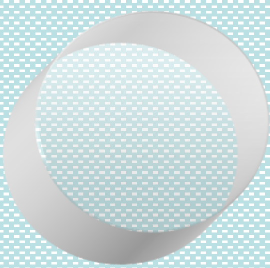
Novel luminescent bulk material:

Rare-earth Ions Doped Transparent Oxyfluoride Glass Ceramics

Combines both advantages from fluoride crystal and oxide glass

Tranditional luminescent bulk materials





Crystal

+: excellent optical spectral properties

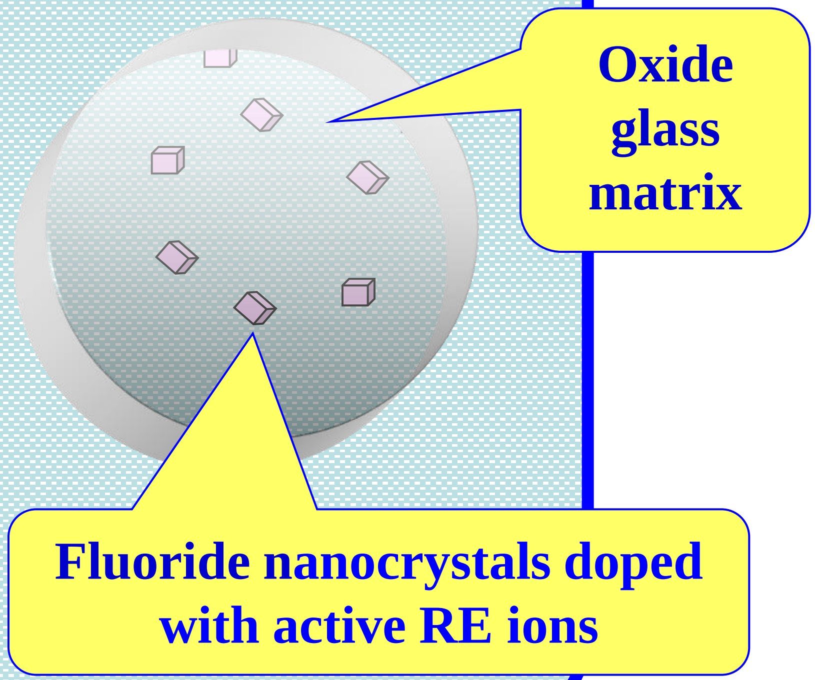
-：high cost，difficult growth to large size

Glass

+: low cost，easy fabrication in large size

-：worse optical spectral properties

Glass ceramic



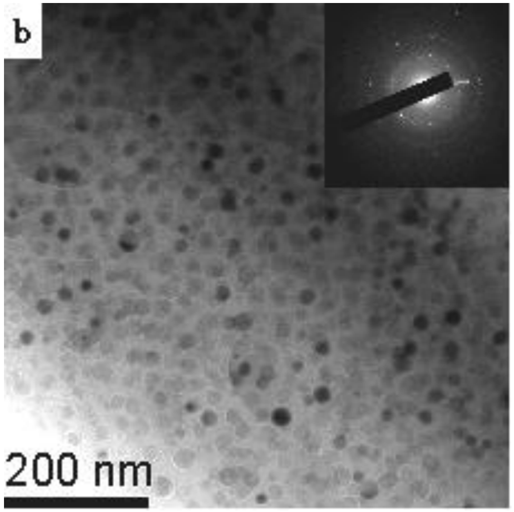
Material's structure determines its performances

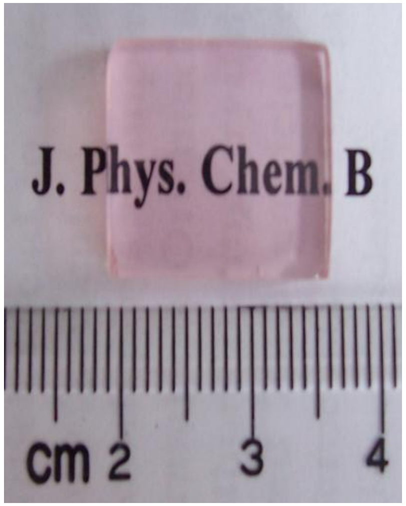
What is favorable microstructure for TGC?

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

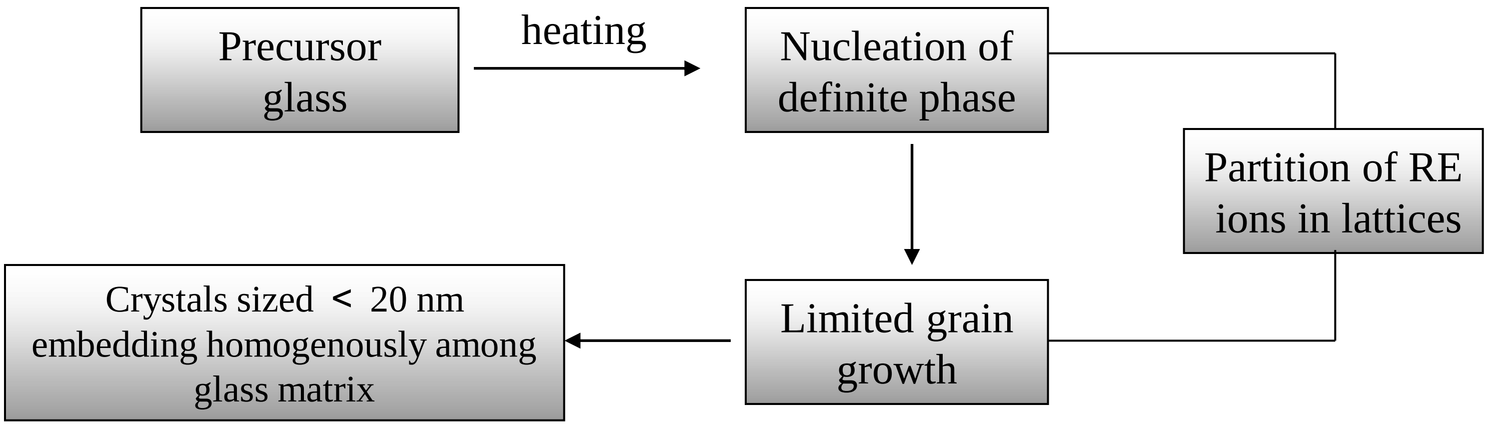
Why oxide glass matrix?

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

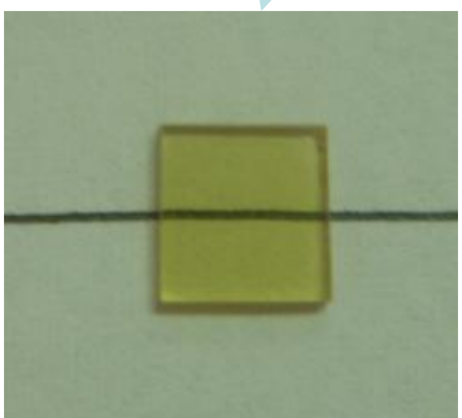


Key points:

- **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 → Poured into pre-heated copper mold and cooled down to room temperature → Annealed to release stress → Precursor glass



Crystallization Kinetics of Glass

Crystallization = Nucleation + Grain Growth

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

$$x = 1 - \exp(-Kt)^{n}$$ JMA equ.

$$K = K_o \exp(-E_a/RT)$$ 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 Ea 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:

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

Ozawa's equation:

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

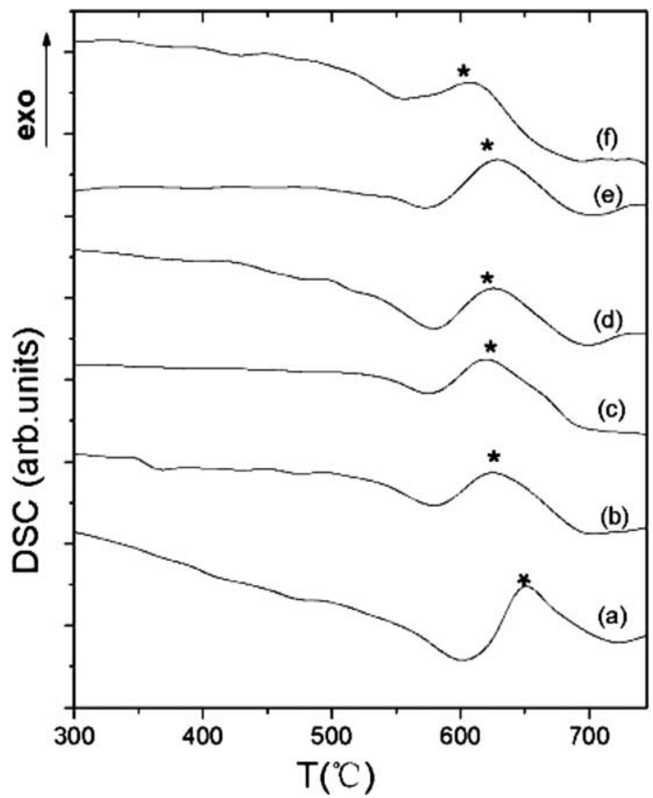
Ozawa's equation:

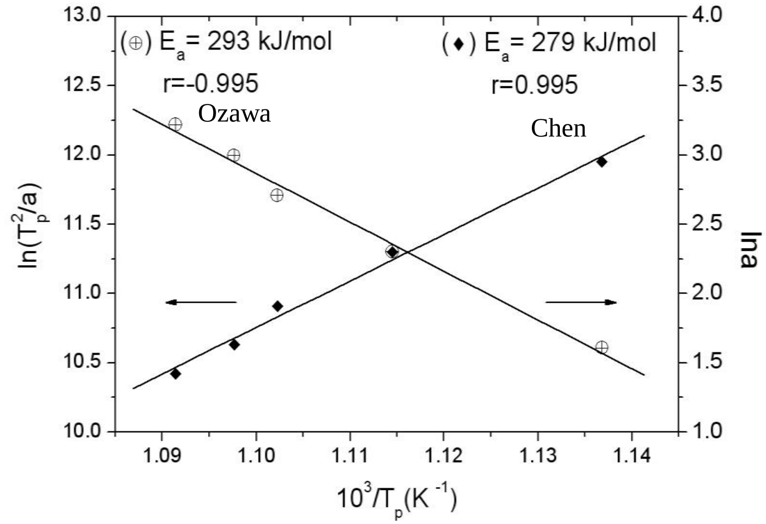
$$\left.\frac{d\{\ln[-\ln(1-x)]\}}{d\ln\alpha}\right|_{Tx} = -n$$

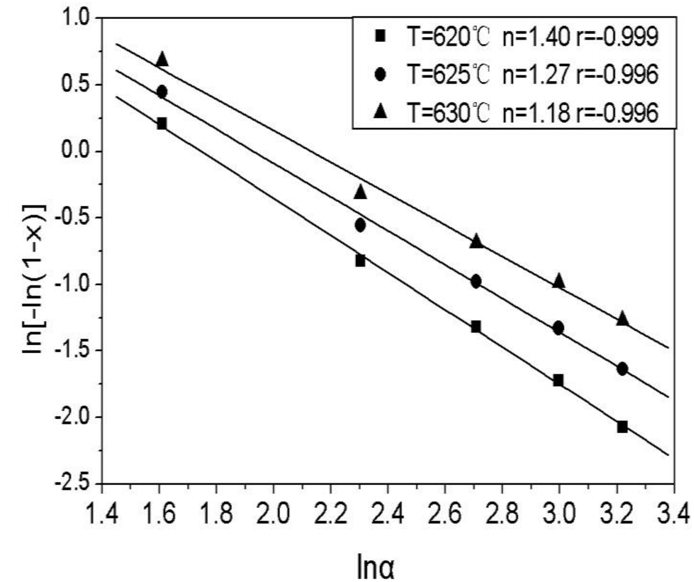
α: heating rate;

T_p: crystallization temperature at a given heating rate;

x: crystallized volume fraction at a fixed temperature T_x with heating rate α.







Example illustrating the determination of E_a and n for crystallization in glass matrix

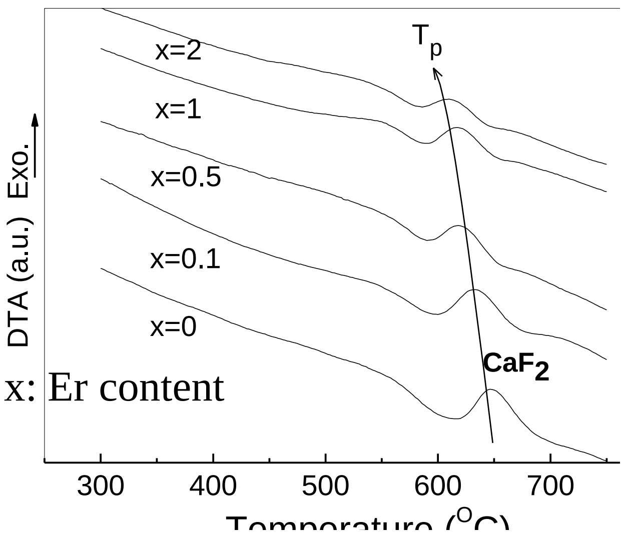
r is the correlative coefficient of least-squares fitting

Various kinds of crystallization mechanisms	n value
(a) polymorphous crystallization, interface controlled growth	
increasing nucleation rate	> 4
constant nucleation rate	4
decreasing nucleation rate	3-4
zero nucleation rate	3
interfacial nucleation (saturated)	1
grain edge nucleation (saturated)	2
(b) diffusion controlled grain growth	
increasing nucleation rate	> 2.5
constant nucleation rate	2.5
decreasing nucleation rate	1.5-2.5
zero nucleation rate	1.5
growth from preexisted precursors	1-1.5
thickening of large plates	0.5
film growth	1
threads growth	2

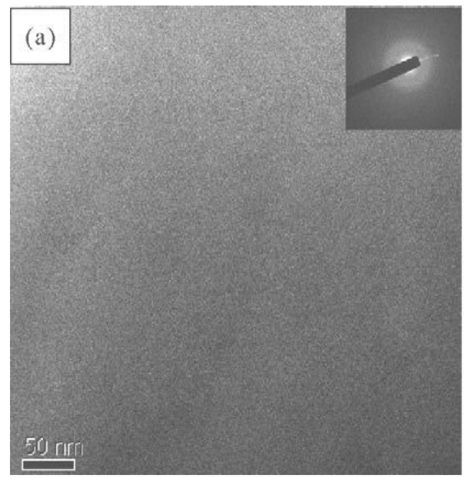
(determined by E_a value)

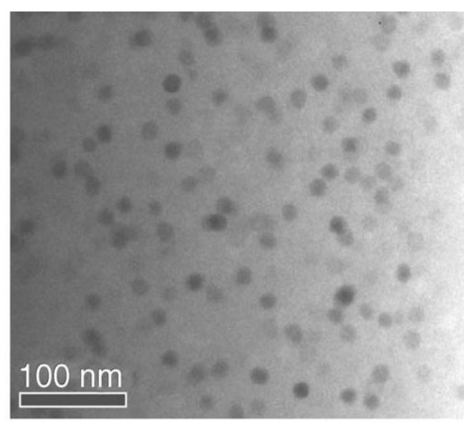
Several examples of crystallization for fluoride nanocrystals in glasses

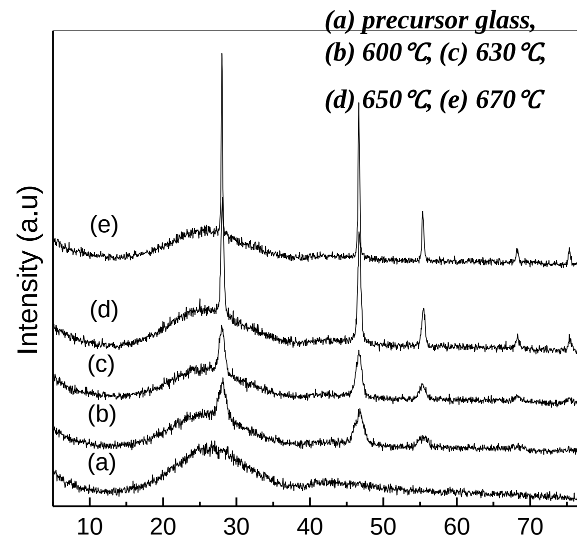
CaF_2:Er contained GC



Er ions acted as nucleation agent to promote crystallization







Heating induced precipitation of CaF_2 nanocrystals

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

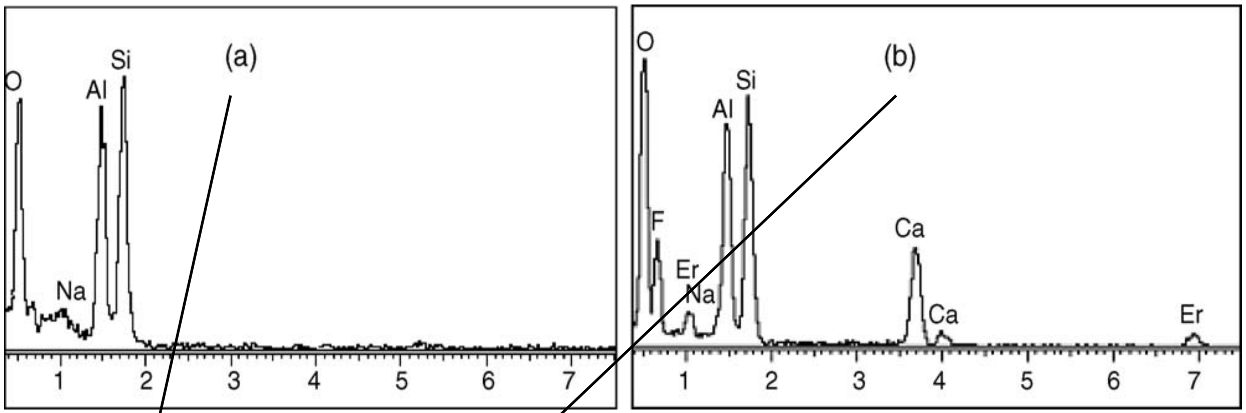
crystllization mechanism of CaF_2

Sample	T_p (℃)	E_a (kJ/mol)		n
		Chen's method	Ozawa's method	
x=0.0	647	299	314	
x=0.1	633			
x=0.5	621	314	329	1.5~1.7
x=1.0	616			
x=2.0	608	332	347	

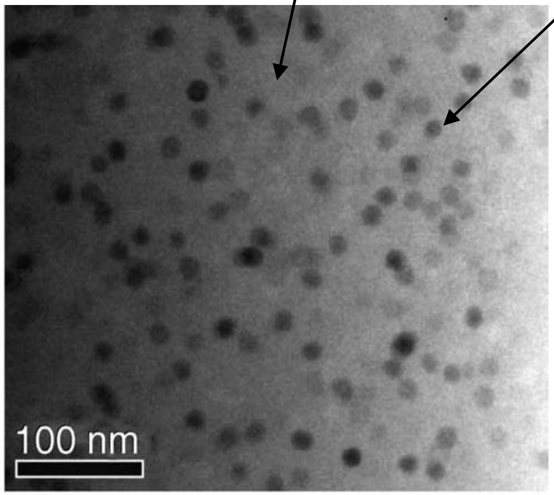
Crystallization was a diffusion-controlled growth from small dimensions with decreasing nucleation rate

- 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.

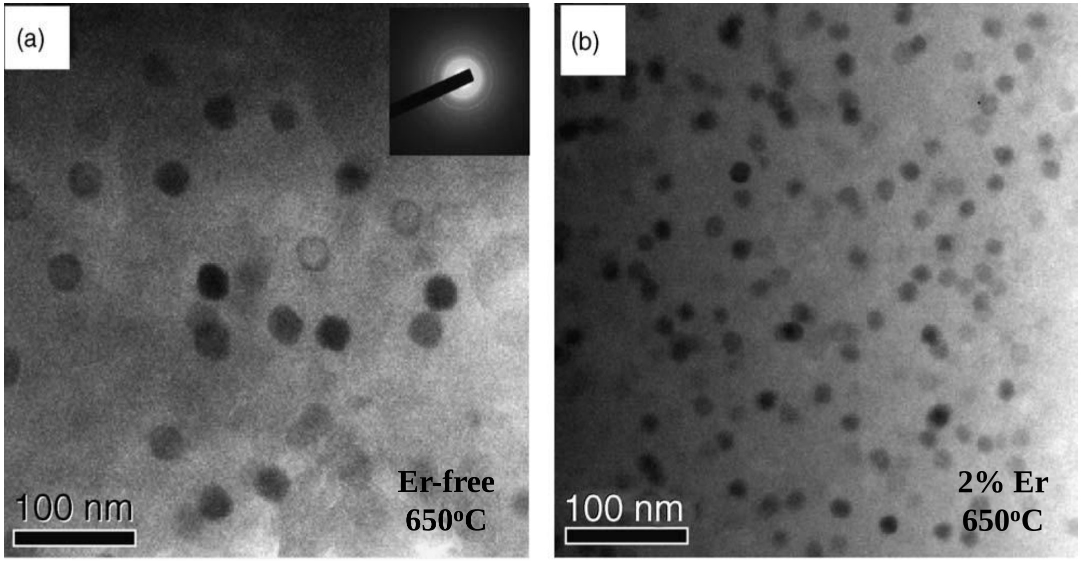
Where were Er ions located ?



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



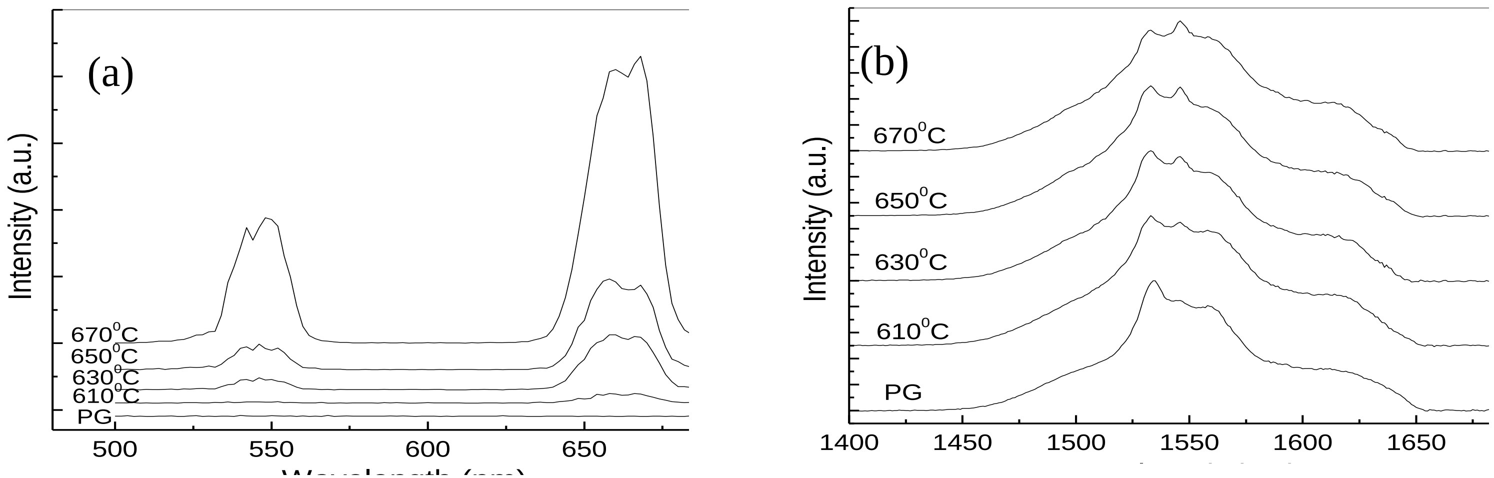
Er ions aggregated in CaF_2 nanocrystals (lattices and surfaces)



After Er-doping, CaF_2 crystal size reduced, while its number density increased.

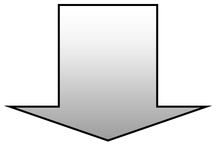
Crystallization Temperature T_p decreased with increasing of Er content x

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.



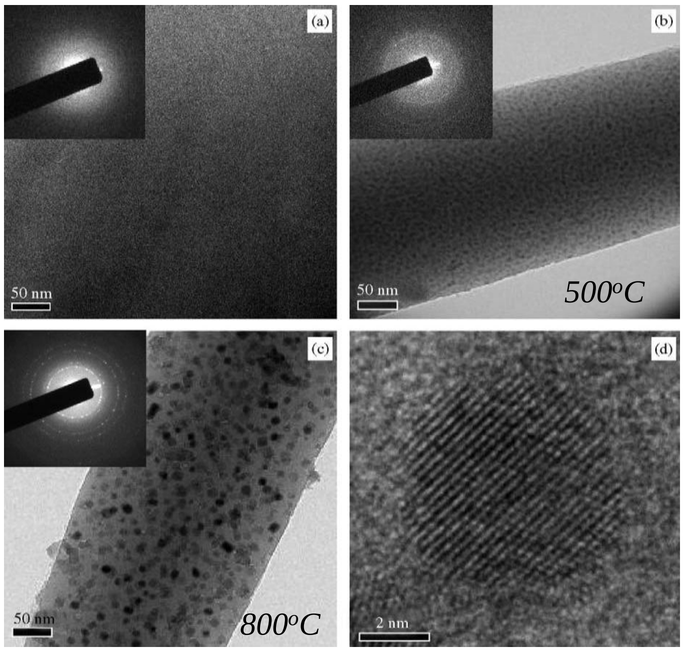
(a) Upconversion emission, and (b) near-infrared emission spectra of glass ceramics under 980 nm excitation

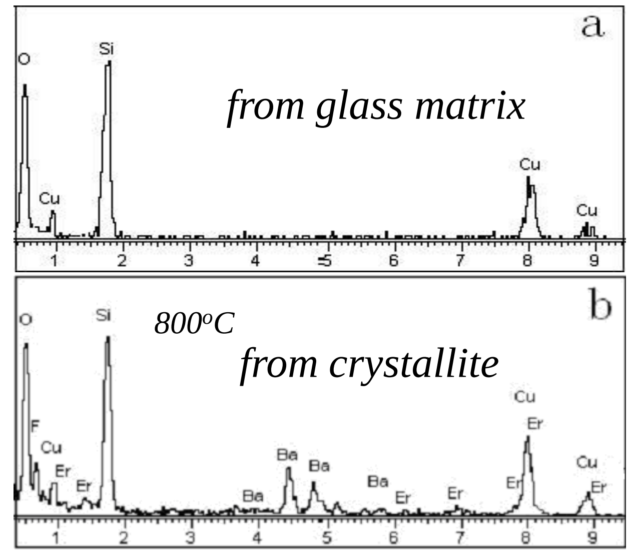
Crystallization induced: Intensification of up-conversion emissions, Spark splitting of emission bands

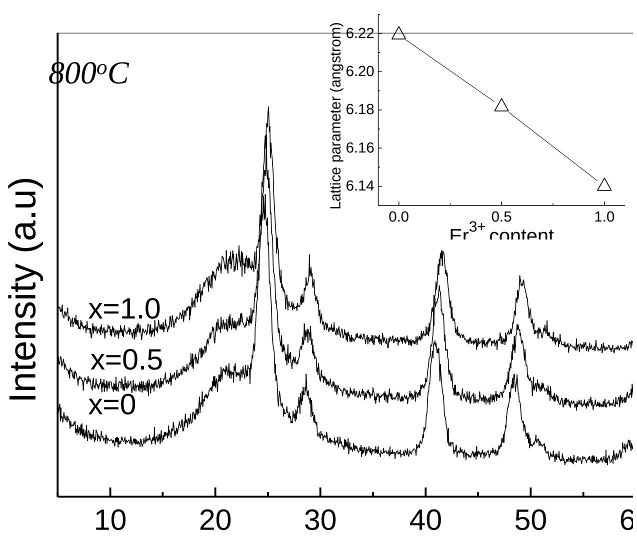


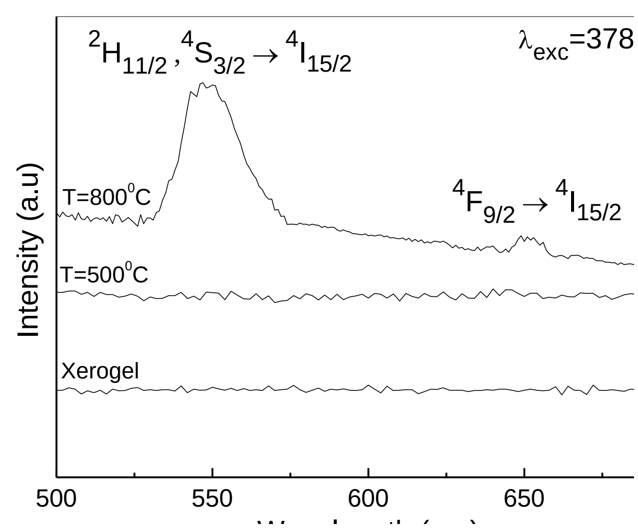
Some of Er ions partitioned in CaF_2 crystalline lattices with low phonon energy

BaF_2:Er contained GC

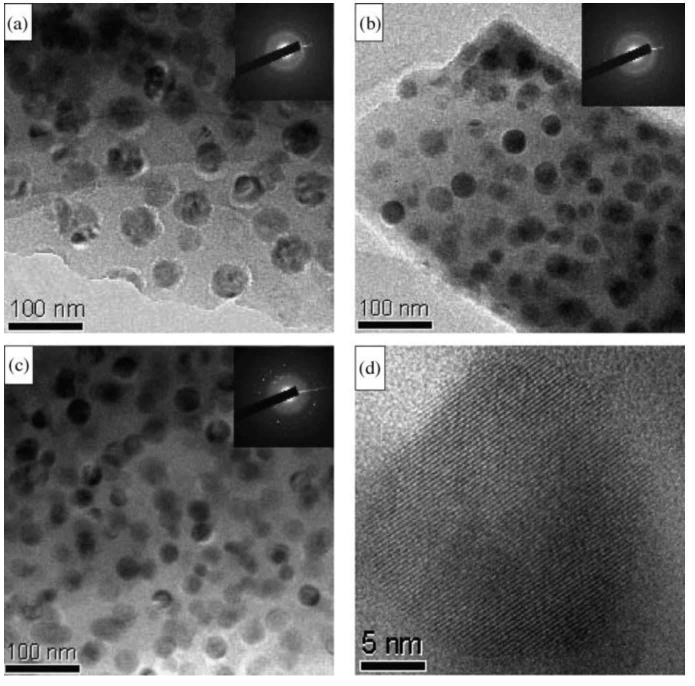




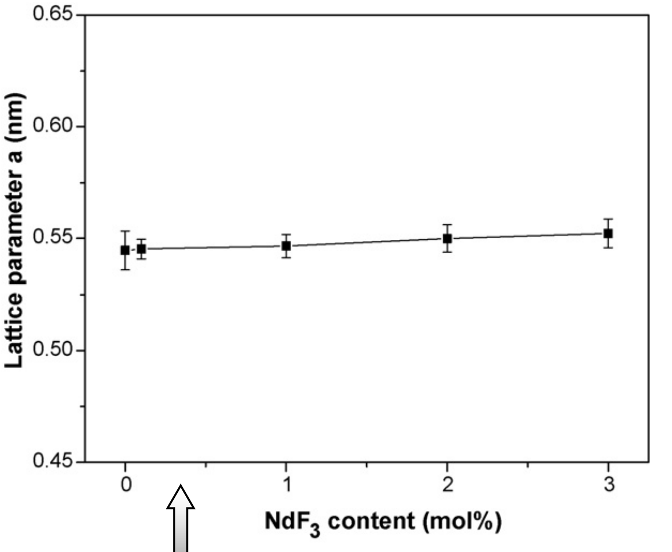




$NaYF_4$:Nd contained GC



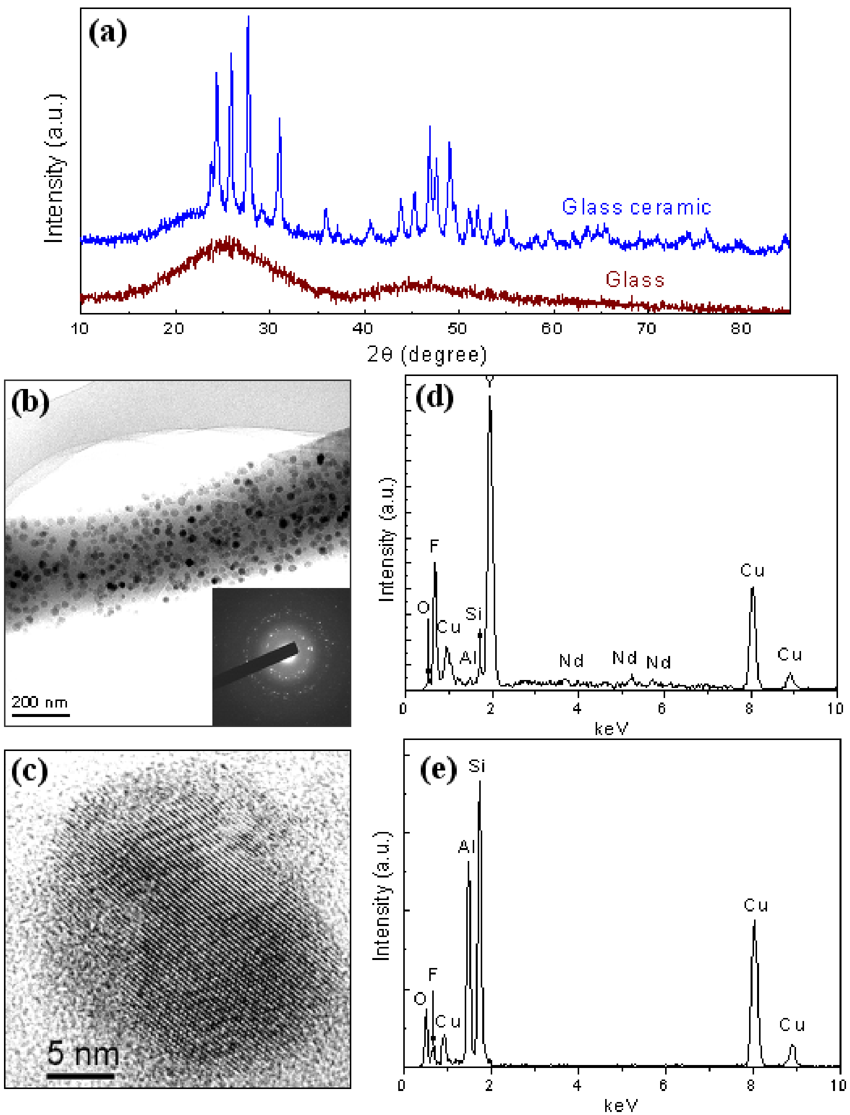
(a) Nd-free; (b) 1% Nd; (c) 3% Nd

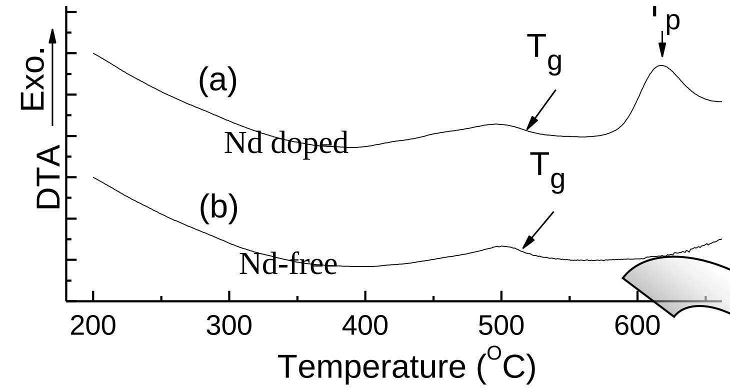


All samples were 620˚C heated

- Kinetic studies reveal the crystallization mechanism being a diffusion-controlled growth of particles with decreasing nucleation rate.
- Nd^{3+} ions acted as nucleation agent and promoted $NaYF_4$ crystallization.
- Expansion of cubic $NaYF_4$ lattice with increasing of Nd^{3+} content indicates incorporation of Nd^{3+} into $NaYF_4$ lattice by substituting Y^{3+}

YF_3:Nd contained GC





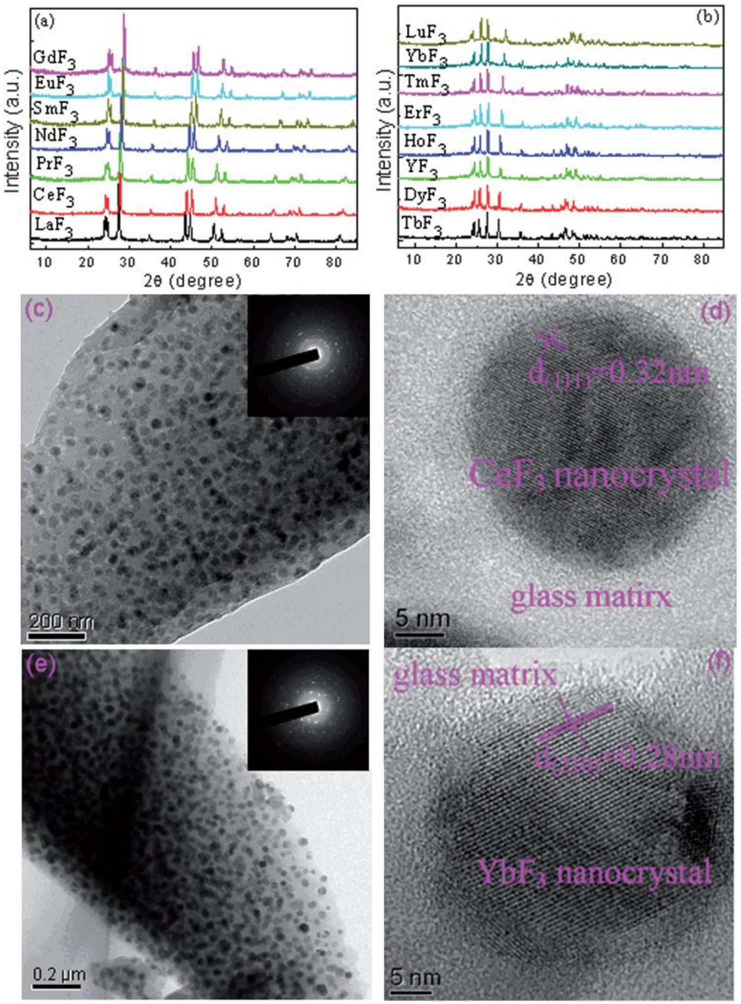
Nd acted as nucleation agent for YF_3 crystallization.

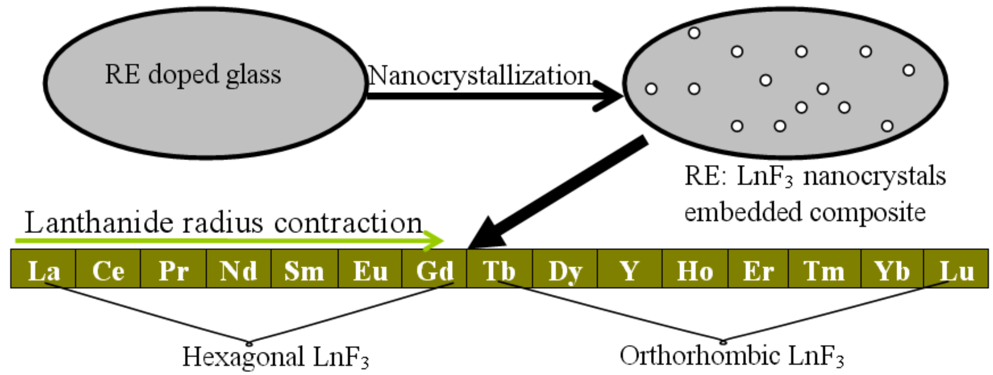
Compared with standard pattern, diffraction peaks of YF_3 nanocrystals shift to the lower angle side

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

Incorporation of Nd^{3+} with radius of 0.126nm into YF_3 by substituting Y^{3+} ions with radius of 0.116nm

General nanocrystallization of LnF_3 (Ln = La–Lu,Y) in SiO_2–Al_2O_3–NaF–LnF_3 glasses



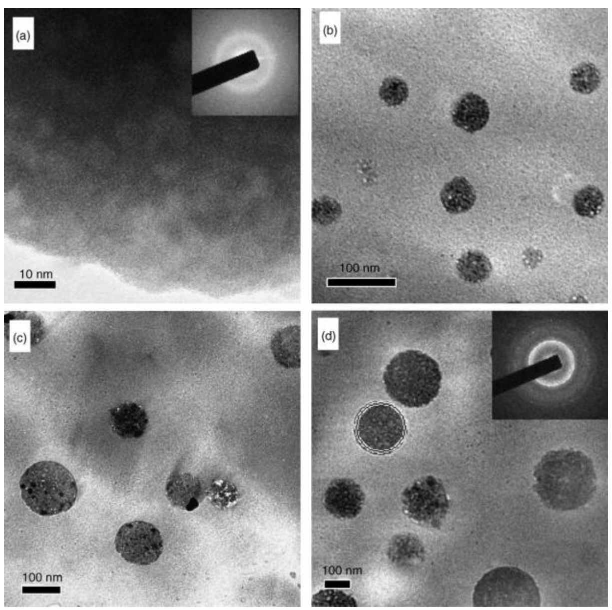


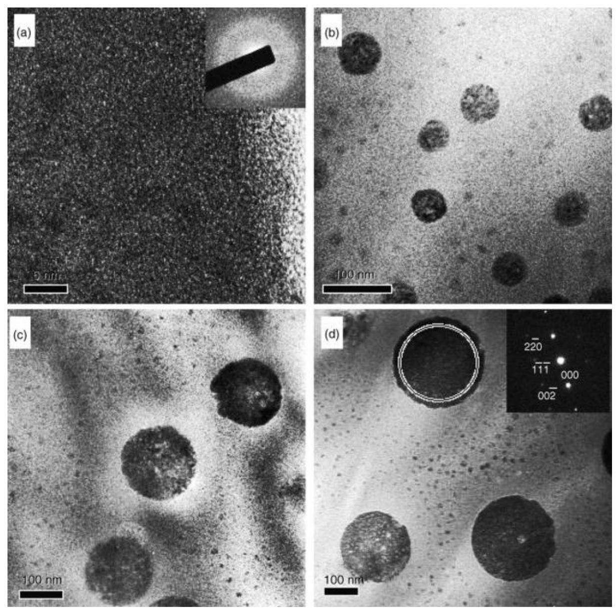
- These fluorides (from LaF_3 to LuF_3) exhibited dimorphism, i.e., the hexagonal structure for those from LaF_3 to GdF_3, and the orthorhombic one for those from TbF_3 to LuF_3 (including YF_3).
- For all the systems, doped RE ions partitioned into the LnF_3 nanocrystals.

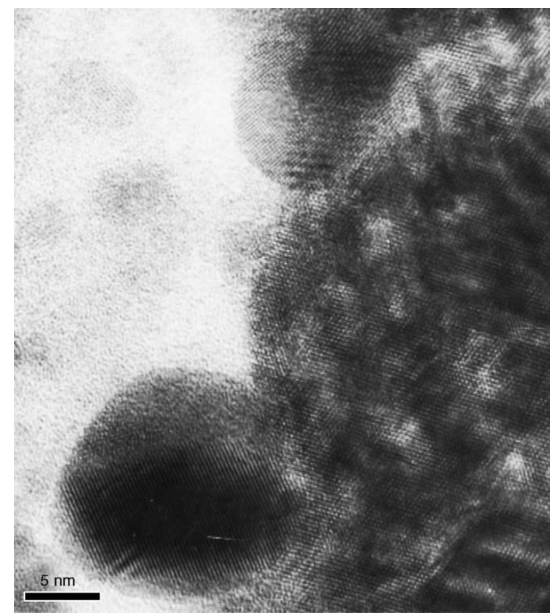
PbF_2:Er contained GC

What were differences?

- **PbF_2 crystallized during melt-quenching ,**
- **Nanocrystals aggregated together ,**
- **Congeries size increased with Er doping ,**
- **Grains grown through Ostwald Ripening**







as-quenched

500°C heat treated

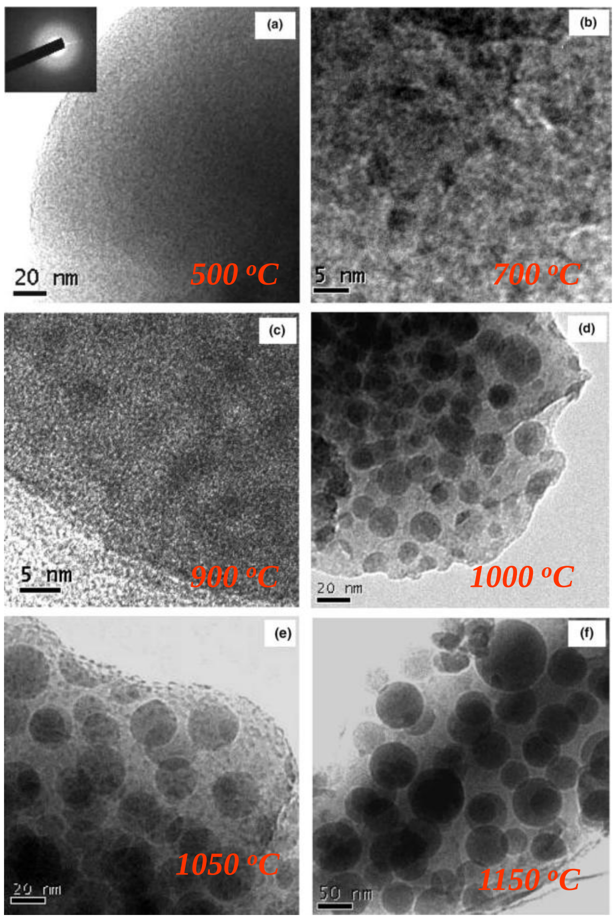
(a) 0 mol% Er, (b) 1 mol% Er, (c) 2 mol% Er and (d) 4 mol% Er

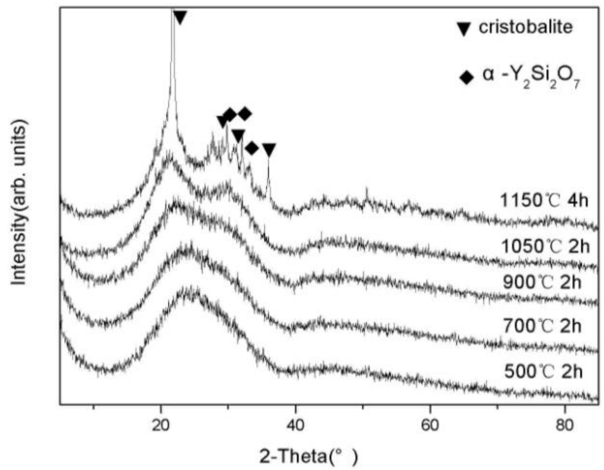
incorporation of small grains to a bigger one

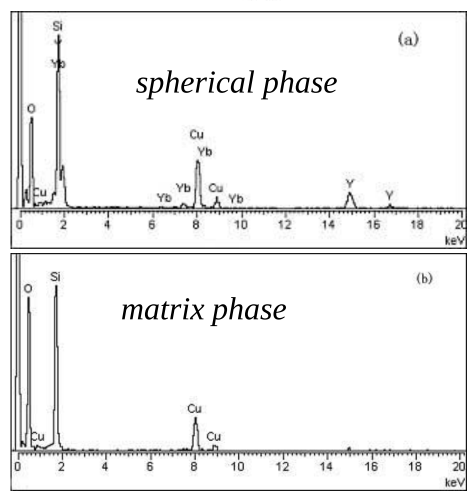
Yb_2O_3–Y_2O_3–SiO_2 GC

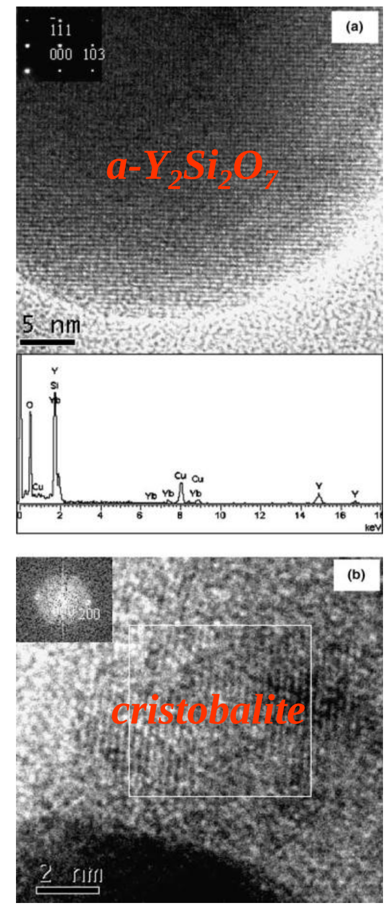
What were differences?

Phase separation determined nucleation and crystallization



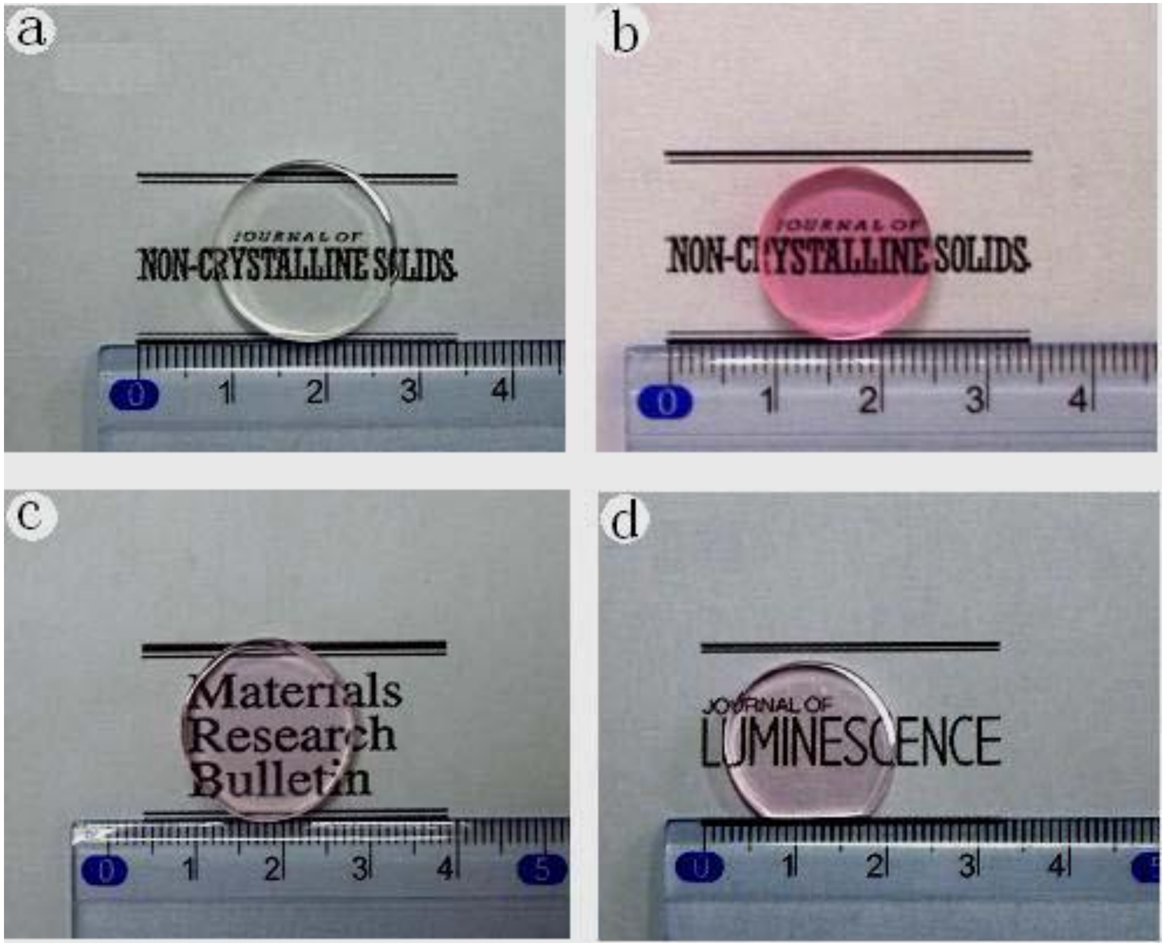






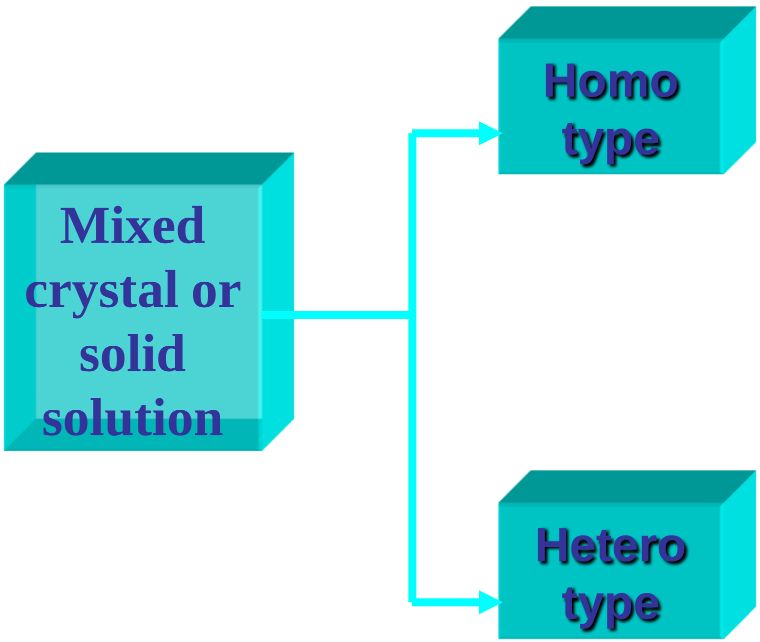

Thanks for attention

Various glass ceramic samples



(a) SiO_2-Al_2O_3-Na_2O-LaF_3； (b) SiO_2-Al_2O_3-Na_2O-LaF_3:Er；
(c) SiO_2-Al_2O_3-CaO-NaF-CaF_2:Er； (d) SiO_2-Al_2O_3-CaO-NaF-CaF_2:Er/Yb

Mixed crystal or solid solution



Similar radius, same structure

$BaSO_4$ - $PbSO_4$

AgCl - AgBr

Different crystalline structure

$BaSO_4$ - CuO