2009 spring

Advanced Physical Metallurgy

“Amorphous Materials”

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Theories for the glass transition

A. Thermodynamic phase transition

- ***Glass transition***

H , V , S : continuous C_p a_T K_T *: discontinuous*

→ by thermodynamic origin, 2nd order transition

→ In fact, it appears on some evidences that the glass transition is not a simple second-order phase transition.

B. Entropy

- *Heat capacity* → dramatic change at Tg
- *Description of glass transition by entropy* (Kauzmann)

$$\boxed{S = \int C_P \, d \ln T}$$

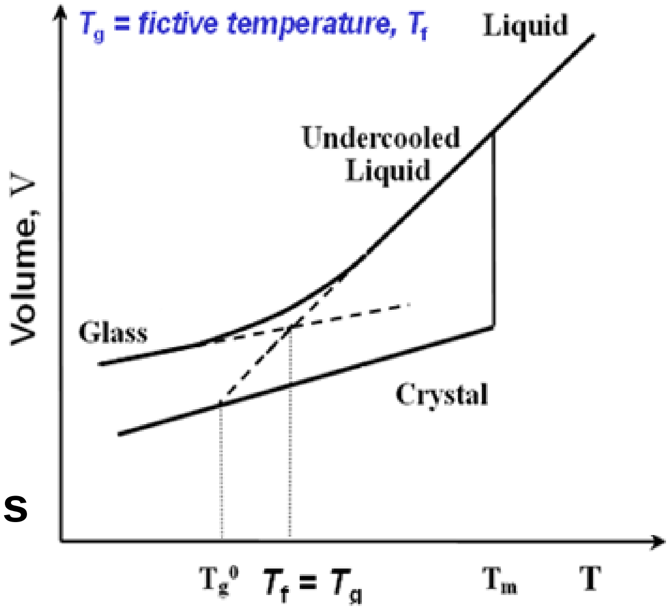
→ *The slow cooling rate, the lower* T_g → T_K *or* T_g^0

→ Measurement of Kauzmann temp. is almost impossible.

(∵ very slow cooling rate → longer relaxation time → crystallization

Theories for the glass transition

C. Relaxation behavior



At high temp. (SCL + Liquid)

Liquid is characterized by equilibrium amorphous structure (metastable to crystalline in SCL).

Below glass transition: frozen-in liquid

→ glass transition is observed when the experimental time scale (1) becomes comparable with the time scale for atom/molecule arrangement (2)

→ If (1) > (2) ➡ liquid/ (1)~(2) ➡ glass transition/ (1) < (2) ➡ glass/

(A concept of glass transition based on kinetic view point)

(property of liquid-like structure suddenly changes to that of solid-like structure)

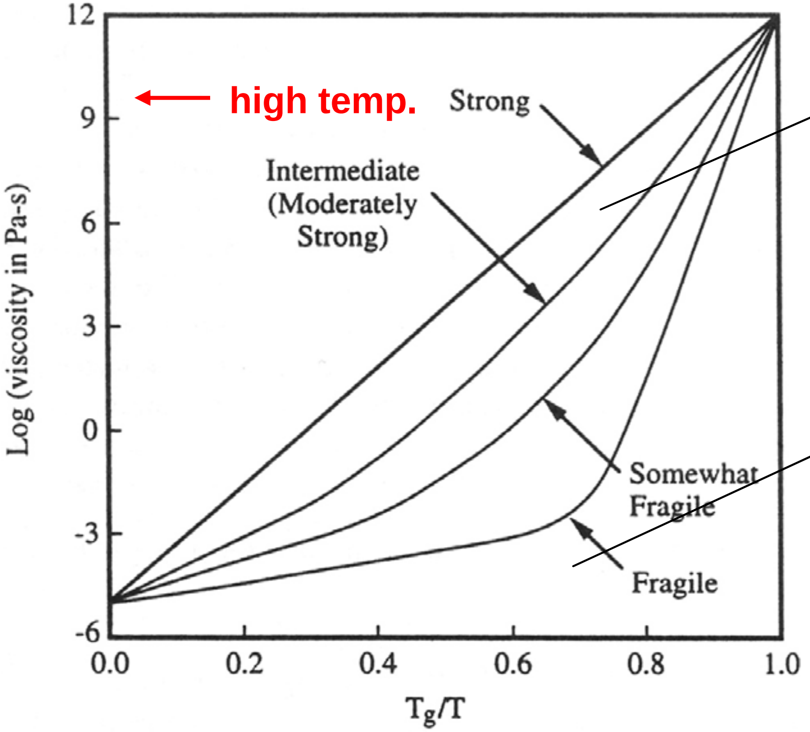
➡ understanding of glass transition from viewpoints of relaxation

d. viscosity

* Another definition of glass transition;

- Viscosity ($10^{12\text{-}13}$ poise)
- most glass forming liquid exhibit high viscosity.
- In glass transition region, viscosity suddenly changes.

→ Fragility concept: Strong vs Fragile



Strong glass **: Arrhenius behavior**

$$\eta = \eta_0 \exp[\frac{E_a}{RT}]$$

→ ***Oxide glass ex) SiO_2, GeO_2***

fragile glass **: Vogel-Fulcher relation**

- deviation from simple Arrhenius behavior

$$\eta = \eta_0 \exp[\frac{B}{T - T_0}]$$

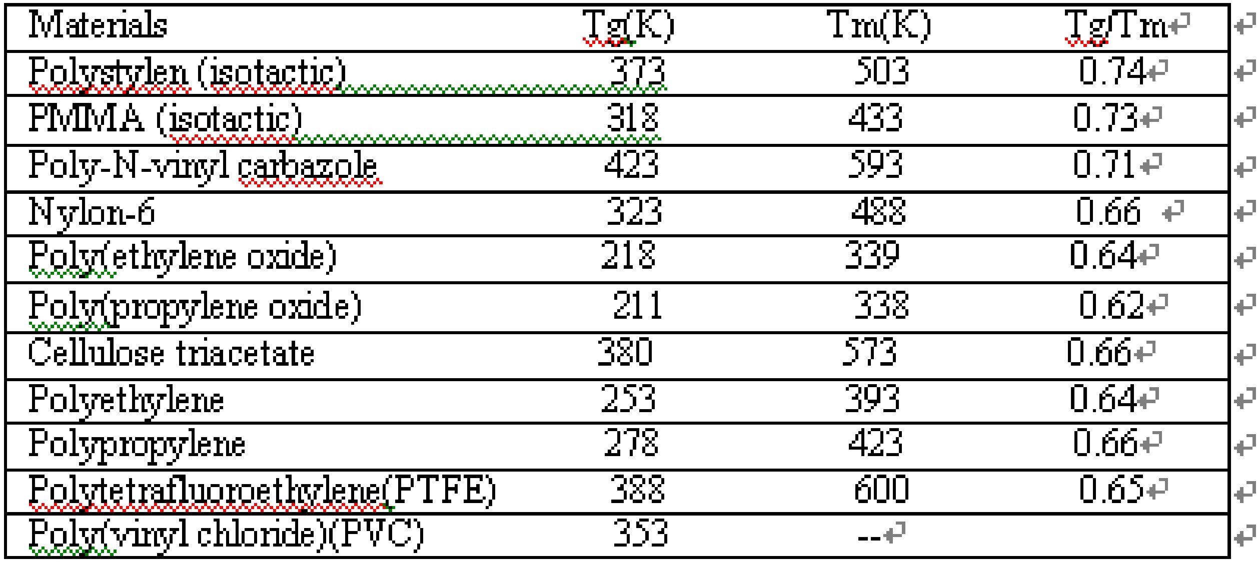
→ ***Ionic system, organic materials***

2.4 Factors that determine the glass transition temperature

→ Which factors affect dominantly Tg?

(1) Tg vs Tm: Tg ≈2/3 Tm

< Organic polymers >



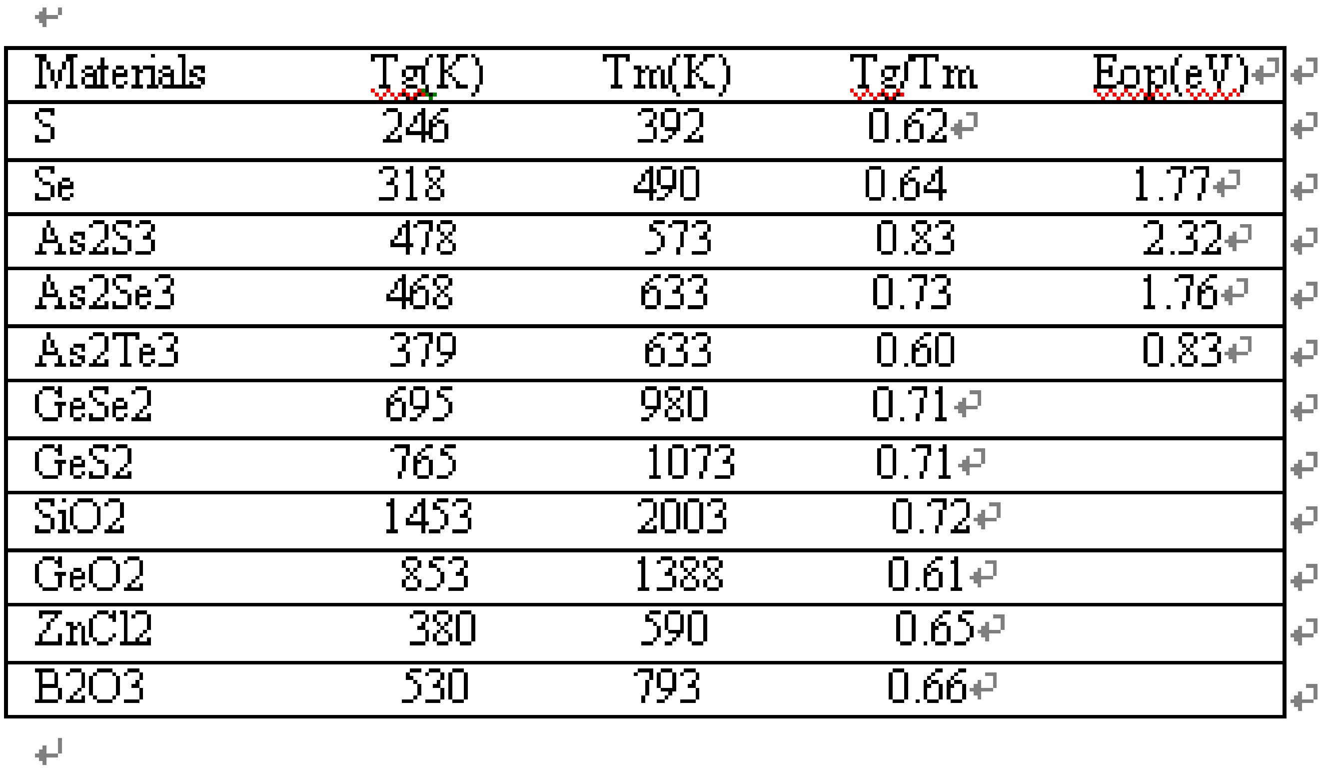
Materials	Tg(K)	Tm(K)	Tg/Tm
Polystylen (isotactic)	373	503	0.74
PMMA (isotactic)	318	433	0.73
Poly-N-vinyl carbazole	423	593	0.71
Nylon-6	323	488	0.66
Poly(ethylene oxide)	218	339	0.64
Poly(propylene oxide)	211	338	0.62
Cellulose triacetate	380	573	0.66
Polyethylene	253	393	0.64
Polypropylene	278	423	0.66
Polytetrafluoroethylene(PTFE)	388	600	0.65
Poly(vinyl chloride)(PVC)	353	--	

- cohesive energy (scaling with boiling temp.)
- band gap (amorphous, semiconductor)
- strength

Eventually, energy for bond breaking or free volume creation?

(2) Tg vs. E_{OPT} : **large E_{OPT} → high Tg**

Materials with strong covalent bonding



Materials	Tg(K)	Tm(K)	Tg/Tm	Eop(eV)
S	246	392	0.62	
Se	318	490	0.64	1.77
As2S3	478	573	0.83	2.32
As2Se3	468	633	0.73	1.76
As2Te3	379	633	0.60	0.83
GeSe2	695	980	0.71	
GeS2	765	1073	0.71	
SiO2	1453	2003	0.72	
GeO2	853	1388	0.61	
ZnCl2	380	590	0.65	
B2O3	530	793	0.66	

Glass transition, melting temperatures, and Eop for some glassy materials

Tg: glass structure (system) dependent

→ more complex…

(3) Composition dependent

ex) As_xSe_{1-x} → Tg did not vary monotonically with composition.

Instead, a maximum in Tg was found for $x \approx 0.4$ (As_2Se_3)

→ Stoichiometric composition

→ Chemically ordered network → **Tg** ⬆

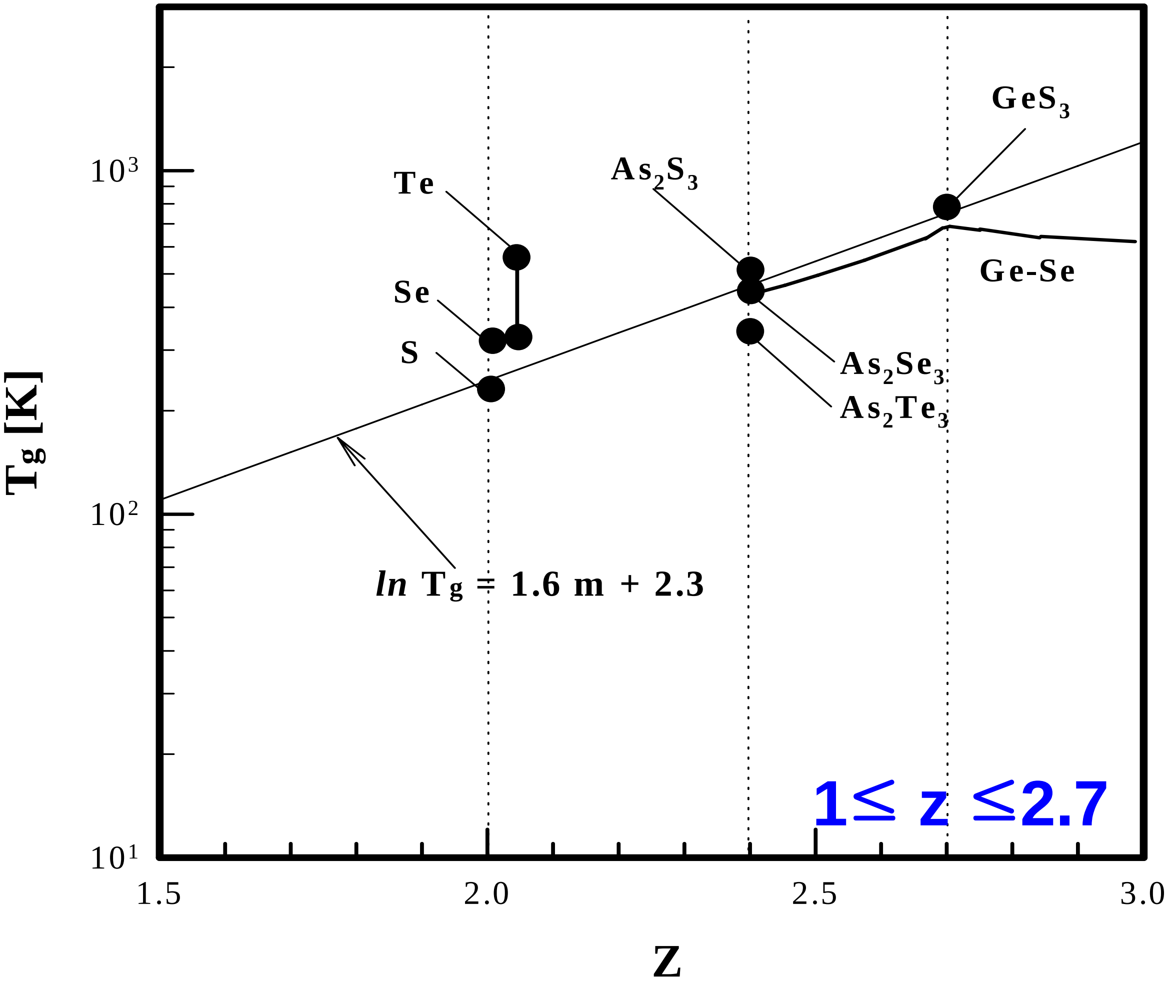
(4) Weak secondary back bone binding structural unit

→ Ruptured preferentially at Tg rather than the primary covalent bonds

→ large-scale motion of clusters or groups of atoms to take place

(5) Empirical relationship between Tg and average coordination # (Z)

$$\longrightarrow \quad \ln T_g \approx 1.6Z + 2.3 \; : \; \mathbf{T_g \equiv \exp(1.6 \bullet z + 2.3)}$$



In conclusion, there appear as yet to be no firm rules for predicting the glass transition, no ready prescriptions with which to calculate Tg for a given glassy material. Tg does not decide single dominant rule.

Advanced Vitreous State: The Structure of Glass

Fundamentals of Glass Formation: Structural and Kinetic Approaches

Glass formation results when the internal structural timescale of the liquid **becomes** or is forced to become significantly longer than the external time scale of the surroundings near the melting or liquidus temperature of the liquid.

Optimizing $\tau_{internal}$ ***for glass formation – Structural approach to glass formation***

- ❑ *Understand and be able to apply the relationships between atomic level structure and ease at which a system will form glass*

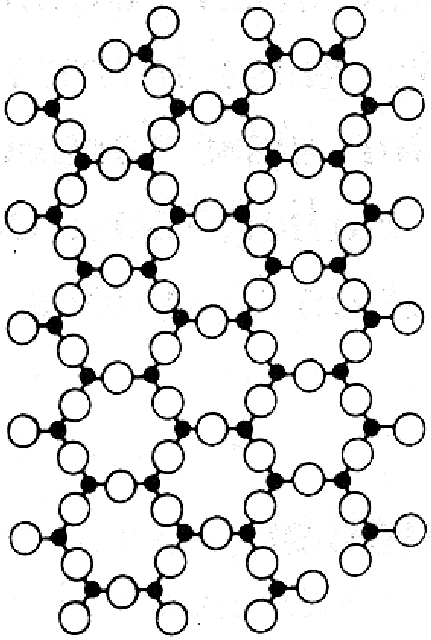
Estimating $\tau_{external}$ ***for glass formation – Kinetic approach to glass formation***

- ❑ *Understand and be able to use nucleation and growth theory*
- ❑ *Understand and be able to use TTT curves*
- ❑ *Understand and be able to calculate critical cooling rates*

Structural Approach to Glass Formation

- Crystalline materials exhibit a periodic array of atoms and/or ions
- Each atom/ion in the material has a specific location that is periodic in the crystalline structure
- Each location can be exactly specified once the crystalline structure is defined
- Defects in the structure occur when the position and atom/ion type do not agree with that prescribed by the crystal structure

A_2O_3 (B_2O_3)

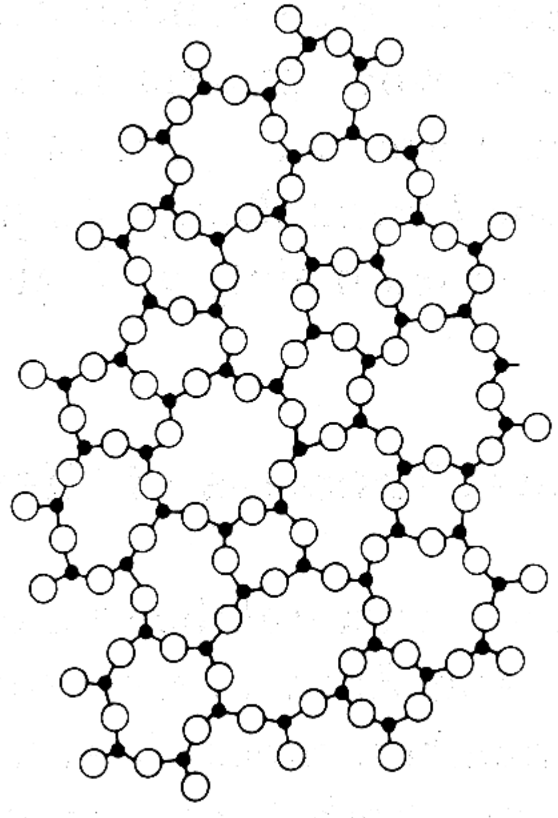


(a)

Structural Approach to Glass Formation

- Amorphous materials lack this long range order
- There is no prescription for which atoms/ions are located at which locations
- However, the energetics of bond formation are very strong
- Atoms will align themselves chemically to:
  - Balance charge in ionic materials
  - Minimize bond energies by filling appropriate bonding orbitals
- Hence, local structure is disordered, but there are still many similarities to the crystalline phase
  - Coordination numbers are ~ same
  - Bond lengths are ~ same
  - Bond Angles are ~ same

A_2O_3 (B_2O_3)



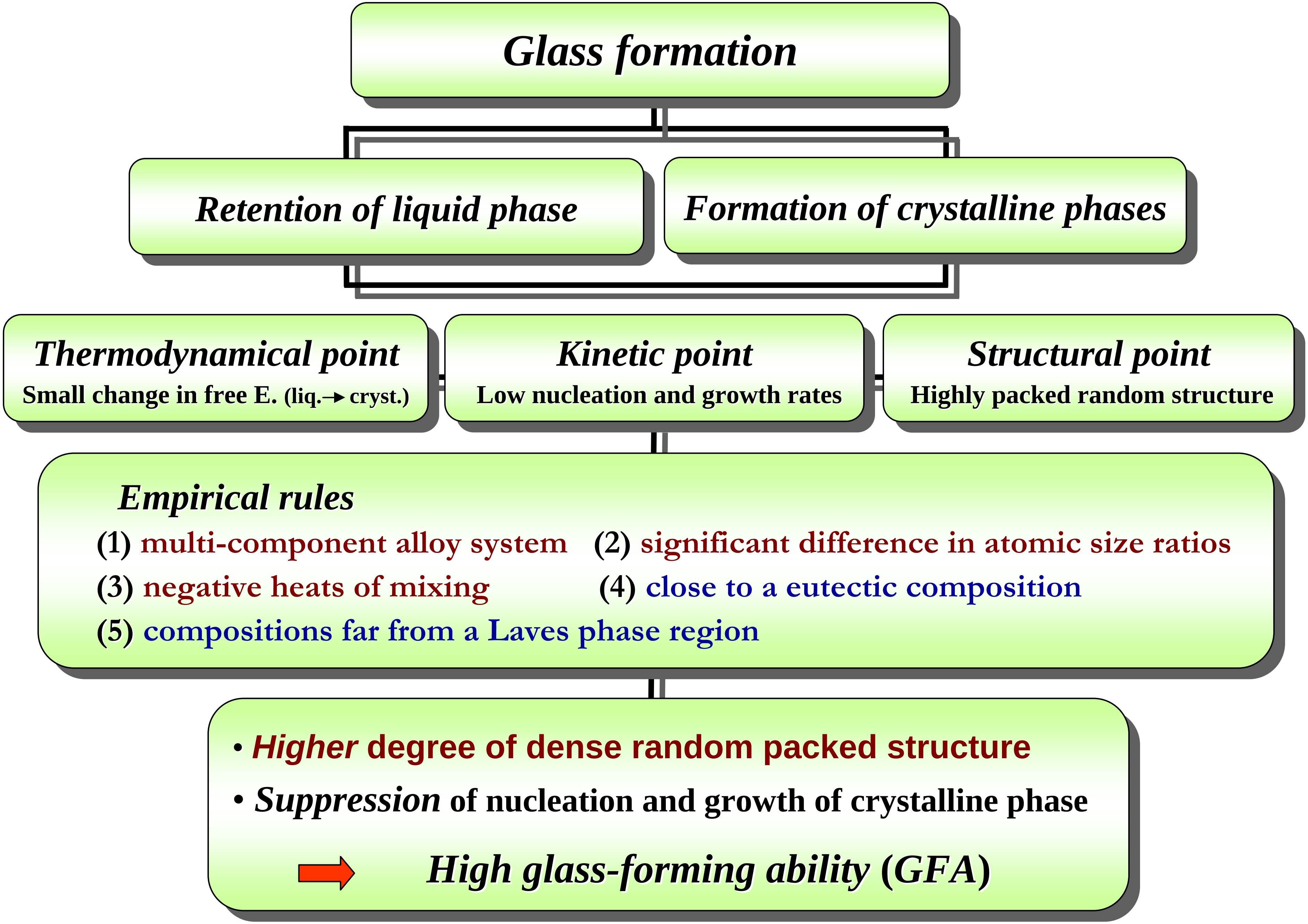
(b)

Structural Approach to Glass Formation

- Glass Formation results when
  - Liquids are cooled to below T_M (T_L) sufficiently fast to avoid crystallization
    - **Nucleation of crystalline seeds are avoided**
    - **Growth of Nuclei into crystallites (crystals) is avoided**
  - Liquid is “**frustrated**” by internal structure that hinders both events
  - Structural Approach to Glass Formation
    - What internal structures promote glass formation?
    - How can structures be developed that increase the viscosity and frustrate crystallization processes?

Structural Approach to Glass Formation

- Using structure to promote glass formation
  - Develop atomic bonding structures in the system that produce large viscosity near the melting point
    - *Silicate liquids and glasses*
      - SiO_2 , $Na_2O + CaO + SiO_2$
  - Develop large molecular structures that due to their size prevent and/or frustrate the organization into the crystalline structure
    - *Polymeric liquids with large polymer chains*
      - $-(CH_2)_n-$
  - Develop complex local and variable structures in the liquid that on cooling have a large number of possible structural motifs to follow and as a result no one structure is favored over another
    - *Molten salt liquids with a number of components*
      - $Ca(NO_3)_2 + KNO_3$



Glass formation

Retention of liquid phase

Formation of crystalline phases

Thermodynamical point

Small change in free E. (liq.→ cryst.)

Kinetic point

Low nucleation and growth rates

Structural point

Highly packed random structure

Empirical rules

(1) multi-component alloy system (2) significant difference in atomic size ratios

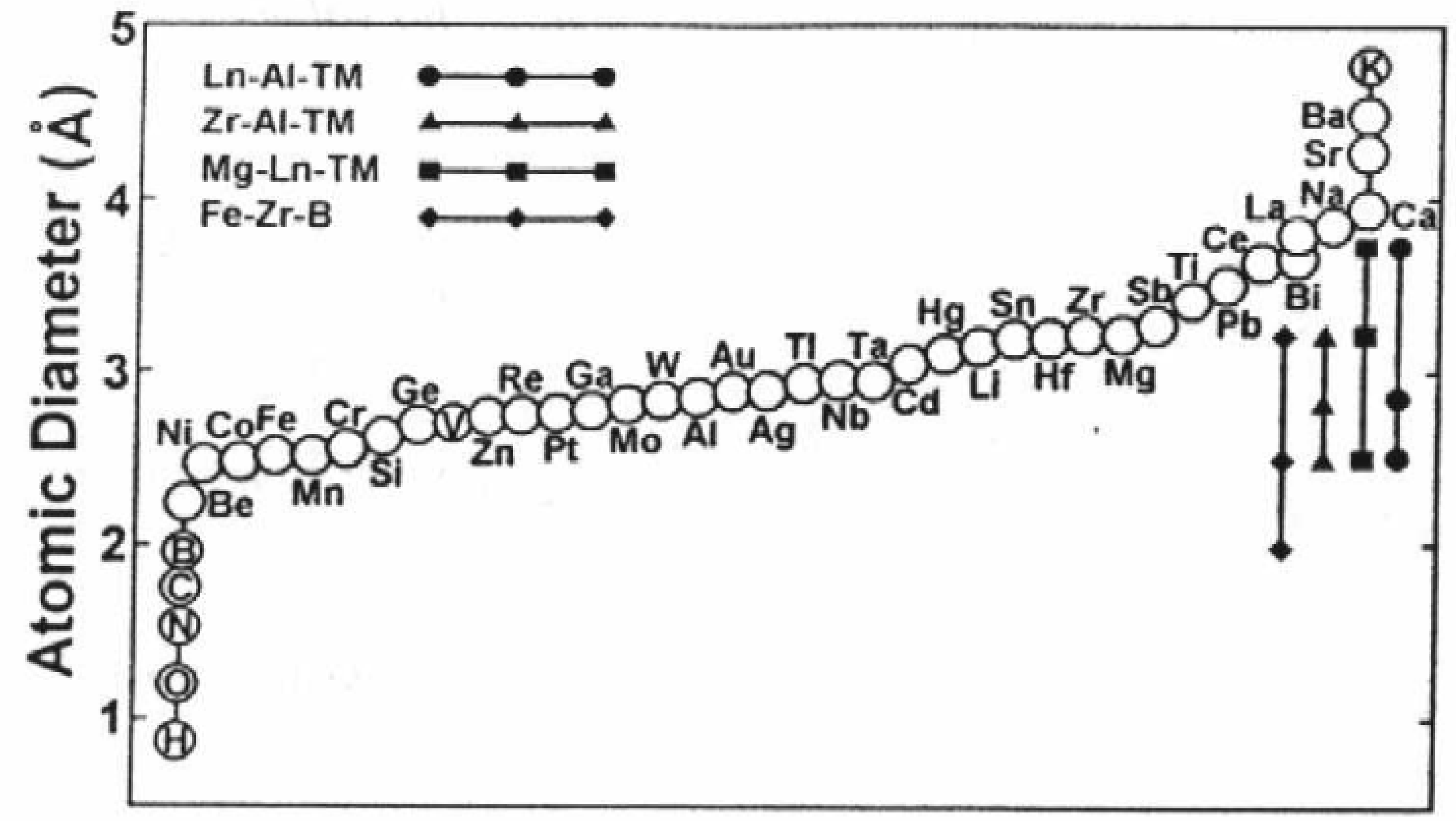
(3) negative heats of mixing (4) close to a eutectic composition

(5) compositions far from a Laves phase region

- ***Higher* degree of dense random packed structure**
- ***Suppression* of nucleation and growth of crystalline phase**

➡ ***High glass-forming ability* (GFA)**

< significant difference in atomic size ratios >



Structural point

- *Metall. & Mater. Trans. A*, **32A, 200 (2001)**

Effect of atomic size difference can be represented as follows;

$$P = C_B\left|\frac{v_B - v_A}{v_A}\right| + C_C\left|\frac{v_C - v_A}{v_A}\right|$$

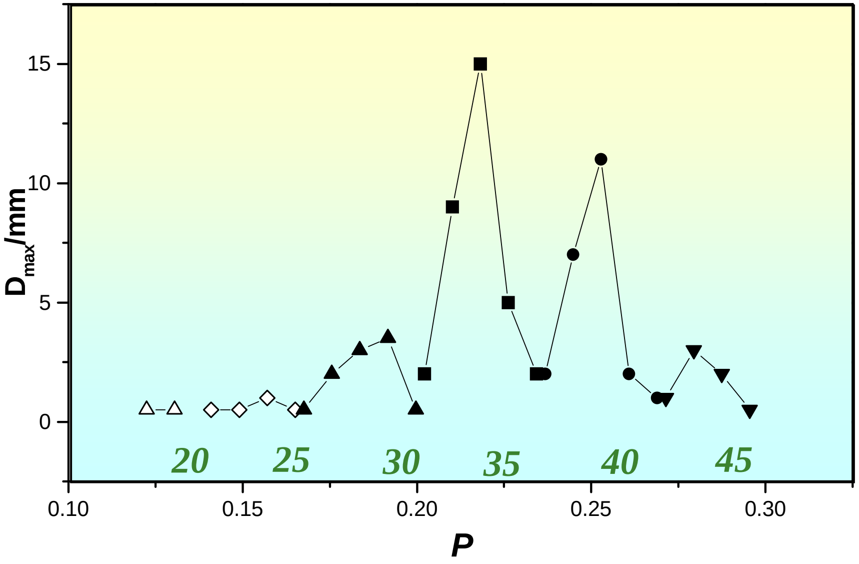
Where, C_i(i=A,B,C) = solute, ν_i = content atomic volume

$$P' = \frac{C_B}{C_B + C_C}\left|\frac{v_B - v_A}{v_A}\right| + \frac{C_C}{C_B + C_C}\left|\frac{v_C - v_A}{v_A}\right|$$

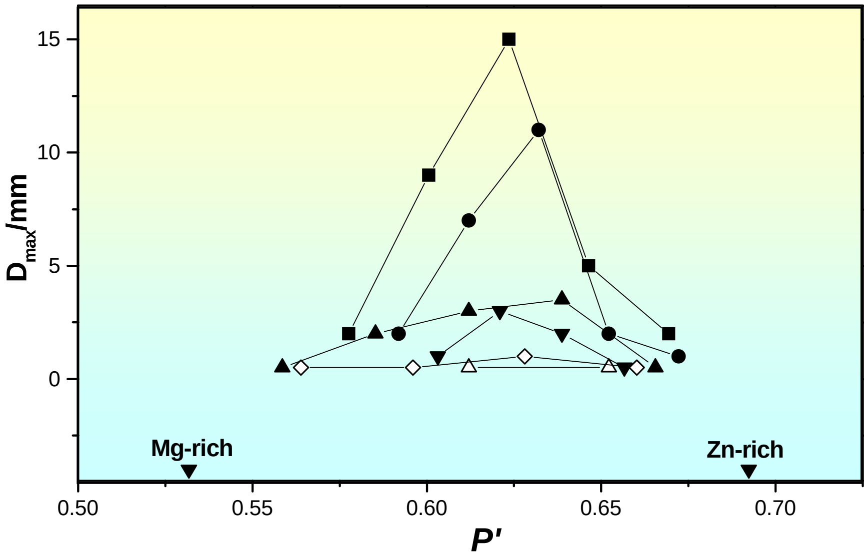
; effective atomic mismatch per solute atom

by dividing by the total amount of solute contents

Ca-Mg-Zn alloy system

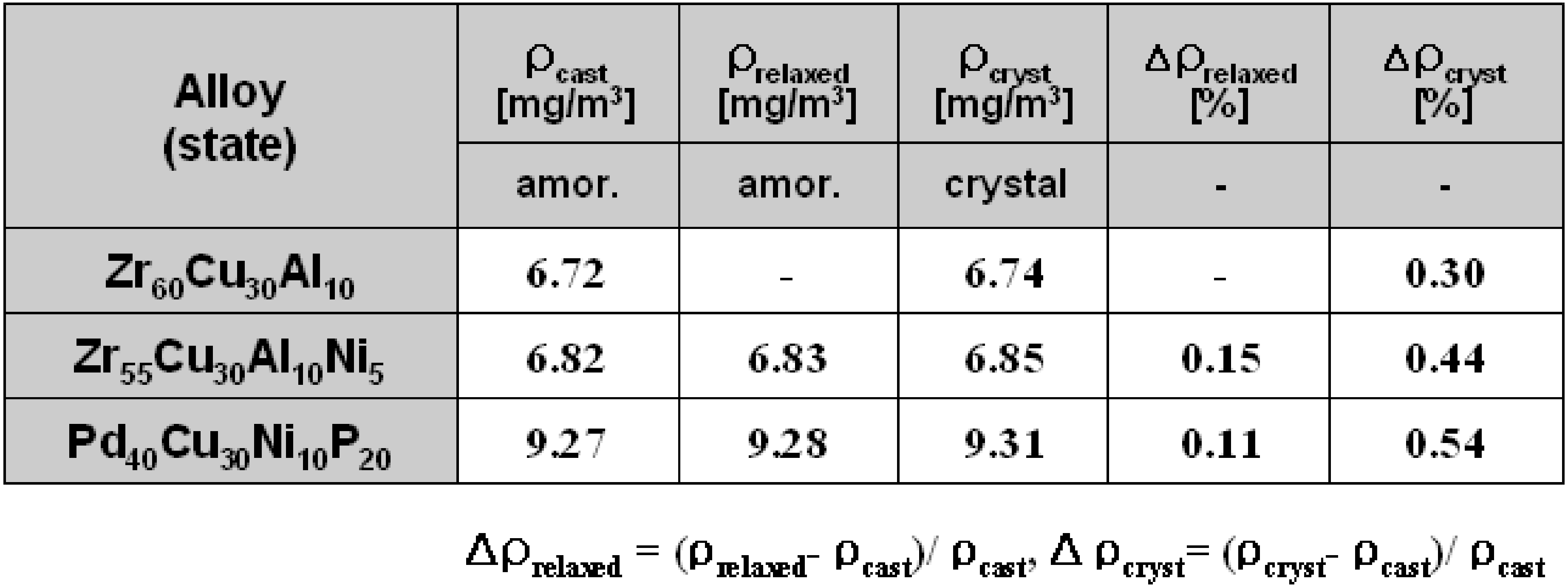


Similar trend of D_{max} with P



Maximum D_{max} at P' ~ 0.625

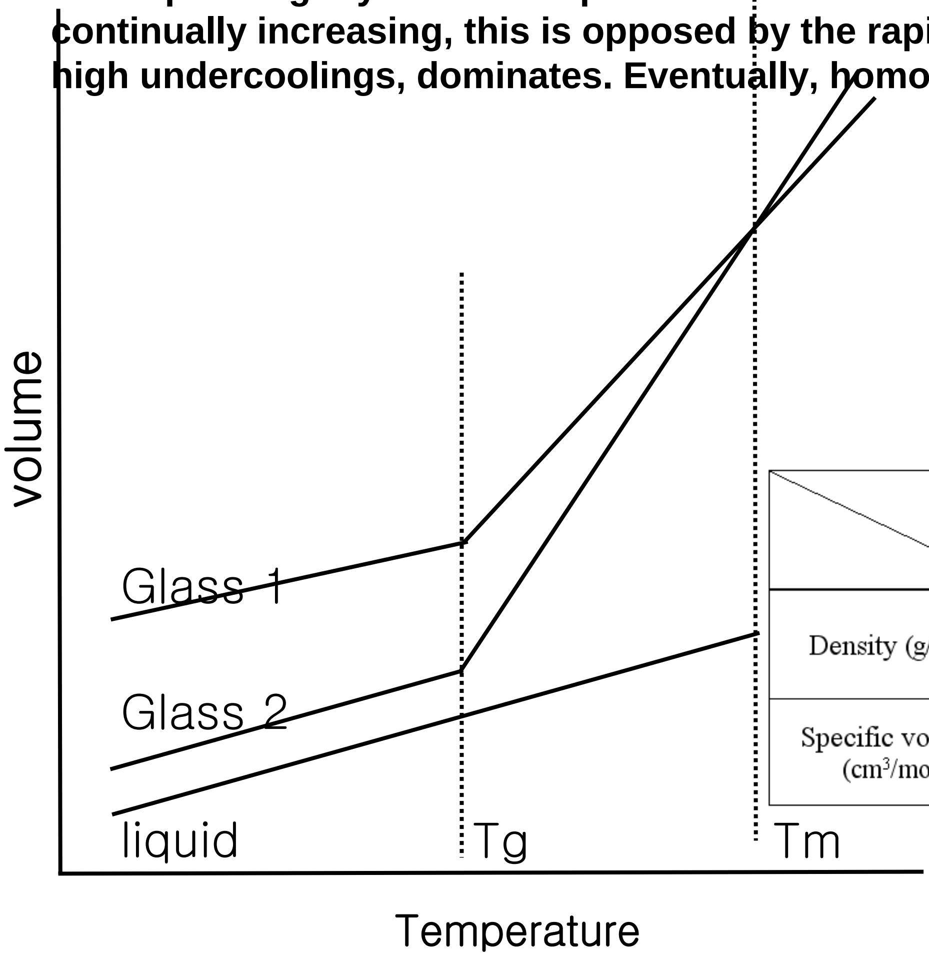
< Density deference between amor. and cryst. state >

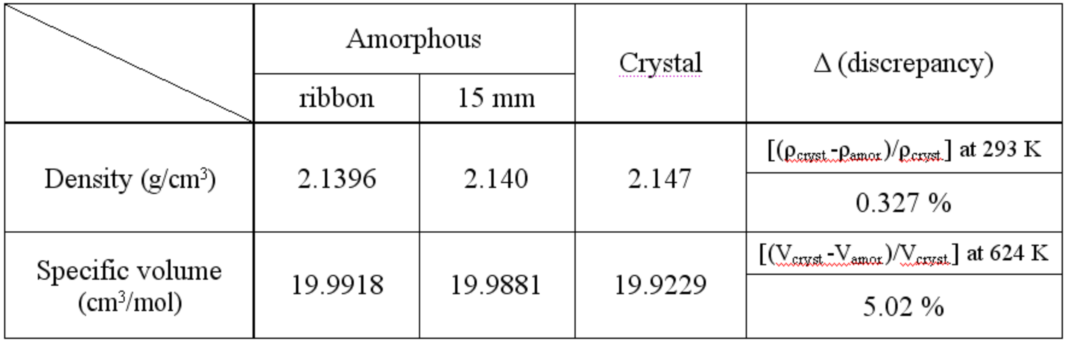


Alloy (state)	ρ_{cast} [mg/m³]	$\rho_{relaxed}$ [mg/m³]	ρ_{cryst} [mg/m³]	$\Delta\rho_{relaxed}$ [%]	$\Delta\rho_{cryst}$ [%]
	amor.	amor.	crystal	-	-
$Zr_{60}Cu_{30}Al_{10}$	6.72	-	6.74	-	0.30
$Zr_{55}Cu_{30}Al_{10}Ni_5$	6.82	6.83	6.85	0.15	0.44
$Pd_{40}Cu_{30}Ni_{10}P_{20}$	9.27	9.28	9.31	0.11	0.54

$\Delta\rho_{relaxed} = (\rho_{relaxed} - \rho_{cast}) / \rho_{cast}$, $\Delta\rho_{cryst} = (\rho_{cryst} - \rho_{cast}) / \rho_{cast}$

The primary crystallization of BMG is known to be controlled by diffusion: it requires long-range atomic diffusion due to a large composition difference between the amorphous phases and its corresponding crystallization products. On cooling, although the driving force for nucleation is continually increasing, this is opposed by the rapidly decreasing atomic mobility which, at very high undercoolings, dominates. Eventually, homogeneously frozen at Tg





	Amorphous		Crystal	Δ (discrepancy)
	ribbon	15 mm		
Density (g/cm^3)	2.1396	2.140	2.147	$[(\rho_{cryst.}-\rho_{amor.})/\rho_{cryst.}]$ at 293 K 0.327 %
Specific volume (cm^3/mol)	19.9918	19.9881	19.9229	$[(V_{cryst.}-V_{amor.})/V_{cryst.}]$ at 624 K 5.02 %

According to the free volume model of a glass, a liquid becomes the glass when the free volume of the liquid is depleted at low temperatures. This idea led to suggest that the glass exhibits more stable state in large αl since the free volume was depleted quickly if αl was large. In Ca-Mg-Zn alloy system, every element has the αl value of over 1.5*10-4 K-1, which is higher value in metallic elements.