## Optical and Photonic Glasses

# Lecture 2:

# Glass Types and Theories of Formation

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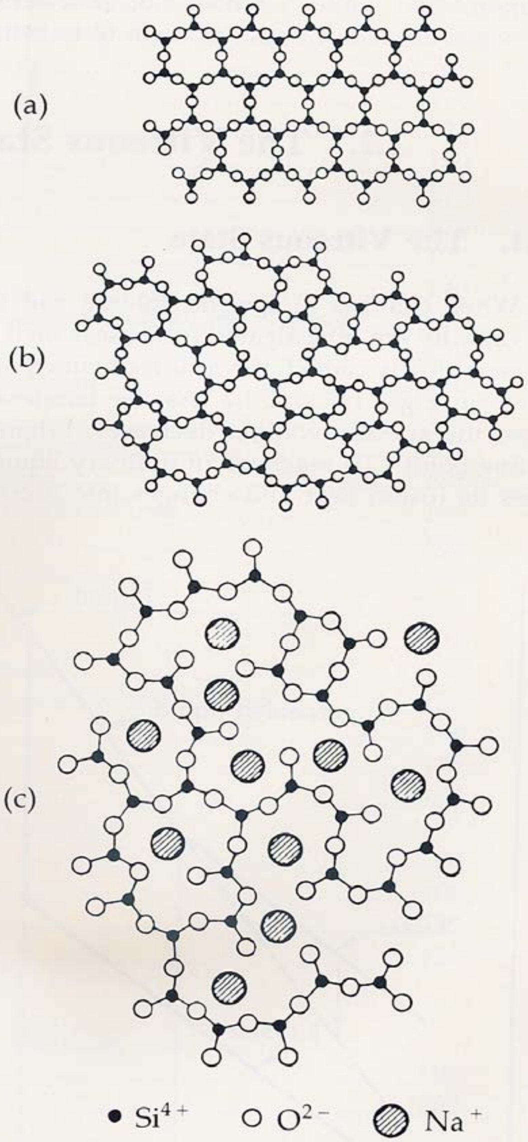
In a multicomponent material like the $SiO_2$–$Na_2O$ glass (c), the question of the **region of glass formation** arises: how much $Na_2O$ can be added to $SiO_2$, while still keeping the glass forming ability of the system?

(Adapted from: *Optical glass*, T.S. Izumitani, Hoya Corporation, 1986)



**1.3. Network structure of $SiO_4^{4+}$ tetrahedrons: (a) quartz crystal, (b) quartz glass, (c) sodium silicate glass (Ref. 5).**

**What is the region of glass formation ?**

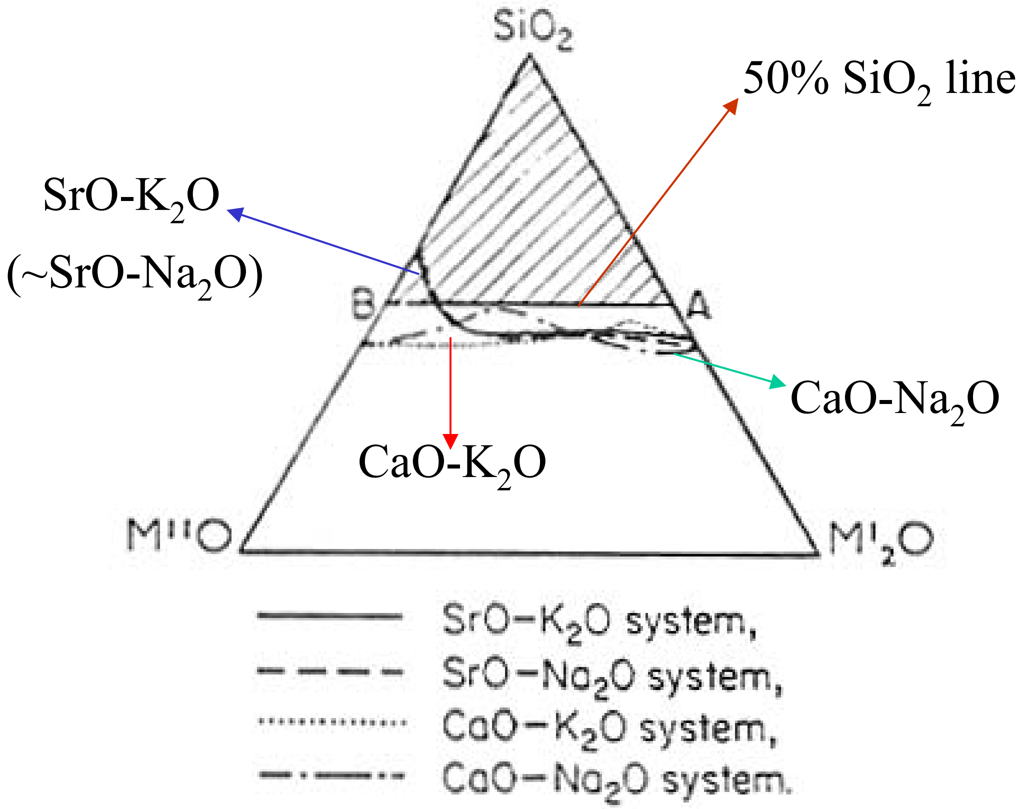
# **Regions of glass formation in oxide glasses** (prepared by melting)

I) Alkali **silicates**:

| | | | |
|---|---|---|---|
| $SiO_2 - Li_2O$ | ~ | 0 – 36 | mol% $Li_2O$ |
| $SiO_2 - Na_2O$ | ~ | 0 – 58 | mol% $Na_2O$ |
| $SiO_2 - K_2O$ | ~ | 0 – 55 | mol% $K_2O$ |
| $- Rb_2O$ | | “ | mol% $Rb_2O$ |
| $- Cs_2O$ | | “ | mol% $Cs_2O$ |

Glasses with > 50 mol% $R_2O$ (< 50 mol% $SiO_2$) are sometimes called “invert glasses”.

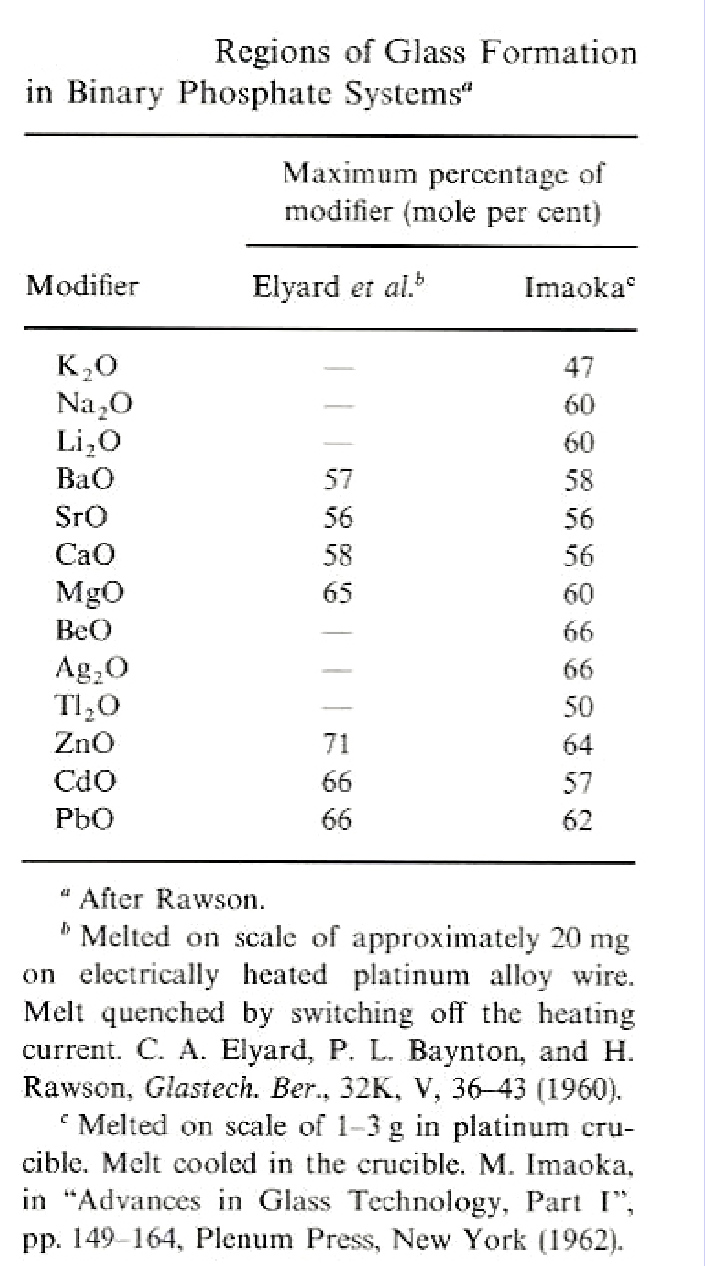
# II) **Ternary** alkali - alkaline earth **silicates**



Glass-formation regions in various ternary silicate glasses. M′ is a monovalent atom, and M″ is a divalent atom. (After M. Imaoka, *Adv. in Glass Tech.*, Part I, p. 149. Plenum Press, New York, 1962. Reproduced with permission of the publisher.)

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

# III) **Phosphate** glasses



Regions of Glass Formation in Binary Phosphate Systems[a]

| | Maximum percentage of modifier (mole per cent) | |
|---|---|---|
| Modifier | Elyard *et al.*[b] | Imaoka[c] |
| $K_2O$ | — | 47 |
| $Na_2O$ | — | 60 |
| $Li_2O$ | — | 60 |
| BaO | 57 | 58 |
| SrO | 56 | 56 |
| CaO | 58 | 56 |
| MgO | 65 | 60 |
| BeO | — | 66 |
| $Ag_2O$ | — | 66 |
| $Tl_2O$ | — | 50 |
| ZnO | 71 | 64 |
| CdO | 66 | 57 |
| PbO | 66 | 62 |

[a] After Rawson.

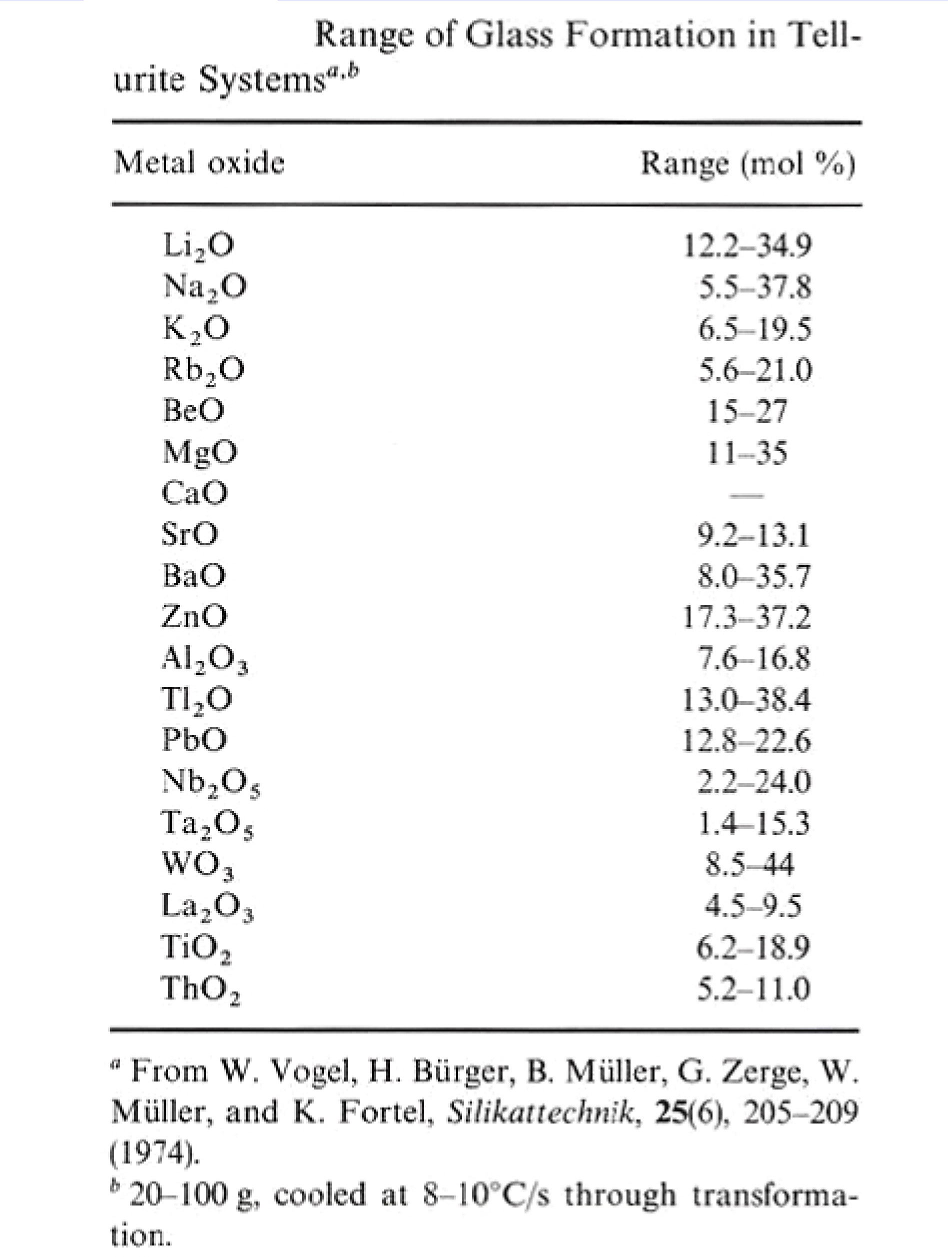
[b] Melted on scale of approximately 20 mg on electrically heated platinum alloy wire. Melt quenched by switching off the heating current. C. A. Elyard, P. L. Baynton, and H. Rawson, *Glastech. Ber.*, 32K, V, 36–43 (1960).

[c] Melted on scale of 1–3 g in platinum crucible. Melt cooled in the crucible. M. Imaoka, in "Advances in Glass Technology, Part I", pp. 149–164, Plenum Press, New York (1962).

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

# IV) **Tellurite** glasses

(Note: pure $TeO_2$ is difficult to obtain as a glass).



Range of Glass Formation in Tellurite Systems[a,b]

| Metal oxide | Range (mol %) |
|---|---|
| $Li_2O$ | 12.2–34.9 |
| $Na_2O$ | 5.5–37.8 |
| $K_2O$ | 6.5–19.5 |
| $Rb_2O$ | 5.6–21.0 |
| BeO | 15–27 |
| MgO | 11–35 |
| CaO | — |
| SrO | 9.2–13.1 |
| BaO | 8.0–35.7 |
| ZnO | 17.3–37.2 |
| $Al_2O_3$ | 7.6–16.8 |
| $Tl_2O$ | 13.0–38.4 |
| PbO | 12.8–22.6 |
| $Nb_2O_5$ | 2.2–24.0 |
| $Ta_2O_5$ | 1.4–15.3 |
| $WO_3$ | 8.5–44 |
| $La_2O_3$ | 4.5–9.5 |
| $TiO_2$ | 6.2–18.9 |
| $ThO_2$ | 5.2–11.0 |

[a] From W. Vogel, H. Bürger, B. Müller, G. Zerge, W. Müller, and K. Fortel, *Silikattechnik*, **25**(6), 205–209 (1974).

[b] 20–100 g, cooled at 8–10°C/s through transformation.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)

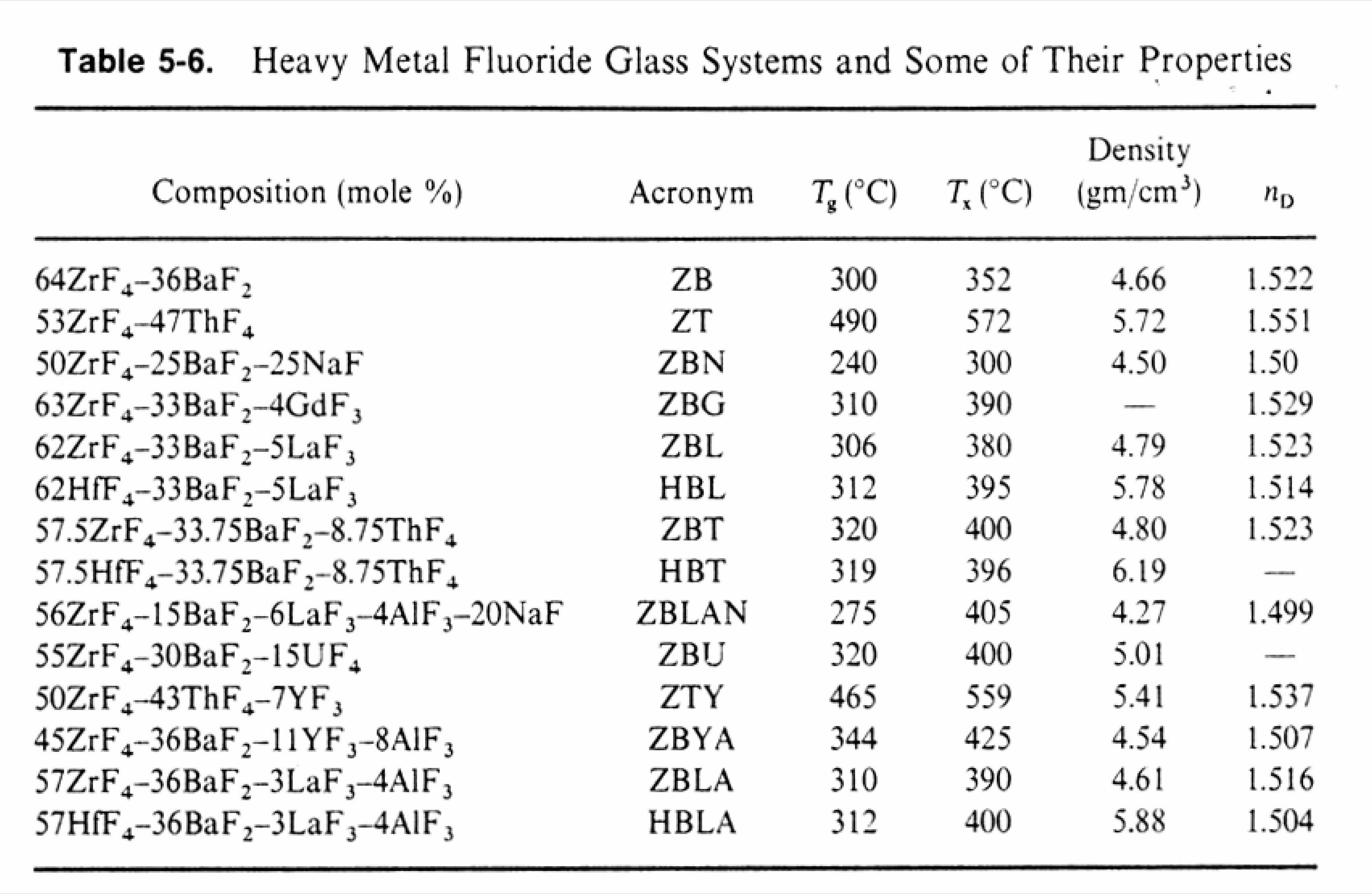


**Table 5-6.** Heavy Metal Fluoride Glass Systems and Some of Their Properties

| Composition (mole %) | Acronym | $T_g$ (°C) | $T_x$ (°C) | Density (gm/cm$^3$) | $n_D$ |
|---|---|---|---|---|---|
| $64ZrF_4$–$36BaF_2$ | ZB | 300 | 352 | 4.66 | 1.522 |
| $53ZrF_4$–$47ThF_4$ | ZT | 490 | 572 | 5.72 | 1.551 |
| $50ZrF_4$–$25BaF_2$–$25NaF$ | ZBN | 240 | 300 | 4.50 | 1.50 |
| $63ZrF_4$–$33BaF_2$–$4GdF_3$ | ZBG | 310 | 390 | — | 1.529 |
| $62ZrF_4$–$33BaF_2$–$5LaF_3$ | ZBL | 306 | 380 | 4.79 | 1.523 |
| $62HfF_4$–$33BaF_2$–$5LaF_3$ | HBL | 312 | 395 | 5.78 | 1.514 |
| $57.5ZrF_4$–$33.75BaF_2$–$8.75ThF_4$ | ZBT | 320 | 400 | 4.80 | 1.523 |
| $57.5HfF_4$–$33.75BaF_2$–$8.75ThF_4$ | HBT | 319 | 396 | 6.19 | — |
| $56ZrF_4$–$15BaF_2$–$6LaF_3$–$4AlF_3$–$20NaF$ | ZBLAN | 275 | 405 | 4.27 | 1.499 |
| $55ZrF_4$–$30BaF_2$–$15UF_4$ | ZBU | 320 | 400 | 5.01 | — |
| $50ZrF_4$–$43ThF_4$–$7YF_3$ | ZTY | 465 | 559 | 5.41 | 1.537 |
| $45ZrF_4$–$36BaF_2$–$11YF_3$–$8AlF_3$ | ZBYA | 344 | 425 | 4.54 | 1.507 |
| $57ZrF_4$–$36BaF_2$–$3LaF_3$–$4AlF_3$ | ZBLA | 310 | 390 | 4.61 | 1.516 |
| $57HfF_4$–$36BaF_2$–$3LaF_3$–$4AlF_3$ | HBLA | 312 | 400 | 5.88 | 1.504 |

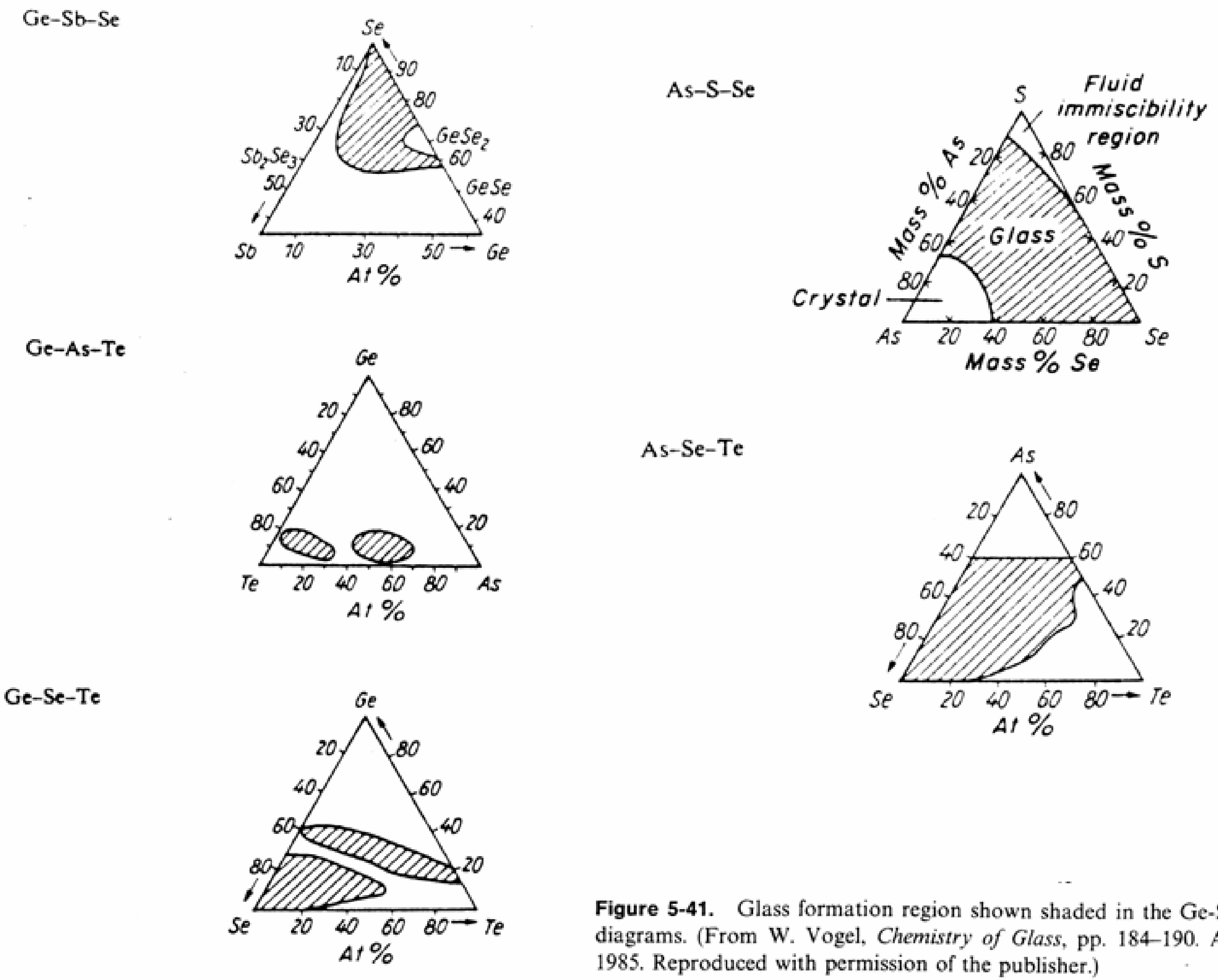


**Figure 5-41.** Glass formation region shown shaded in the Ge-Sb/As-S/Te ternary diagrams. (From W. Vogel, *Chemistry of Glass*, pp. 184–190. Amer. Ceram. Soc., 1985. Reproduced with permission of the publisher.)

## V) **Halide glasses**

Binary fluorozirconates: ~ 50 - 70 mol% $ZrF_4 – BaF_2$

Zinc halide-based glasses: ~ 50 - 60 mol% $ZnBr_2$ – KI

## VI) **Chalcogenide** glasses:

| | | | |
|---|---|---|---|
| As – S – Se | system: | large glass-forming | region |
| As – Se – Te | “ | “ | “ |
| Ge – Sb – Se | “ | smaller | “ |

## Theories of glass formation

There is not yet a single theory which is able to predict and specify which **materials** and under what **conditions** are able to form glasses.

There are, however, three theories (or *models*, rather) which encompass most of the relevant aspects which are known to lead to glass formation:

A) Structural theory of glass formation, proposed by W.H. Zachariasen in 1932 (J. Am. Chem. Soc. 54(1932)3841).

B) Energy criterion of K.H. Sun (1947).

C) Kinetic theory of glass formation (Turnbull and Cohen, 1960).

## A) **Zachariasen**’s theory (oxide glasses)

This theory, strictly applicable to oxide glasses only in its original form, sometimes referred to as the *crystallochemical theory*; it led to the model known as the 3 – D continuous random network (3-D CRN) model.

Basic postulates:

-interatomic forces similar in glass and corresponding crystal

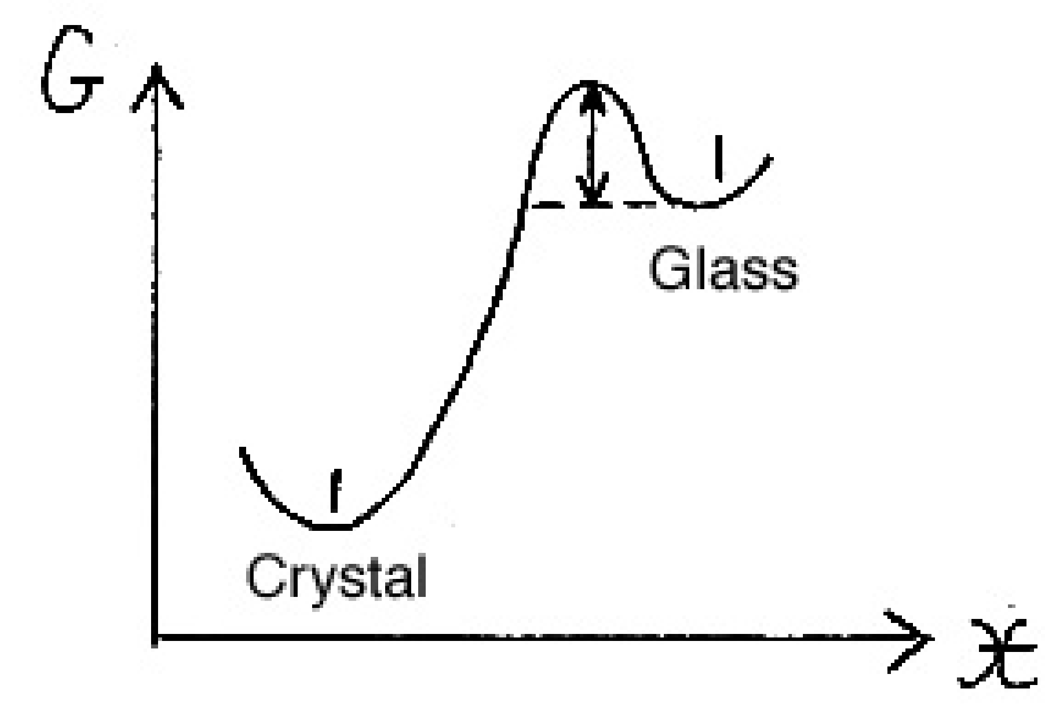
-glass is in a slightly higher energy state (next slide)

-nearest neighbor coordination polyhedra similar in glass and crystal

-nature of interatomic bonds similar in glass and corresponding crystal

The glass is in a higher energy state, compared to the corresponding crystal.

This can be considered a metastable state, in the sense that a certain thermodynamic energy barrier exists (related to the activation energy for crystal growth) for the glass to crystallize. Such energy is provided when the glass is heated above its temperature of onset of crystallization (obtainable from a DSC, or DTA, run).



## **Zachariasen**’s **rules**:

1) each oxygen atom in a glass is bonded only to one or two glass-forming cations (e.g. $Si^{4+}$);

2) the coordination number (CN) of the glass-forming cation is small: 3 or 4;

3) the oxygen coordination polyhedra share corners, but not edges or faces;

4) the polyhedral structural units form a **3-D continuous random network** in which every polyhedron shares at least 3 corners with its neighbors.

## Limitations of Zachariasen's rules

- apply only to oxide glasses (silica, silicates, …)

- there are several exceptions to the rules, such as:

  - non-oxide glasses
  - CN > 4 (e.g. fluoride and metallic glasses)
  - chain-like glass structures (e.g., metaphosphate glasses)

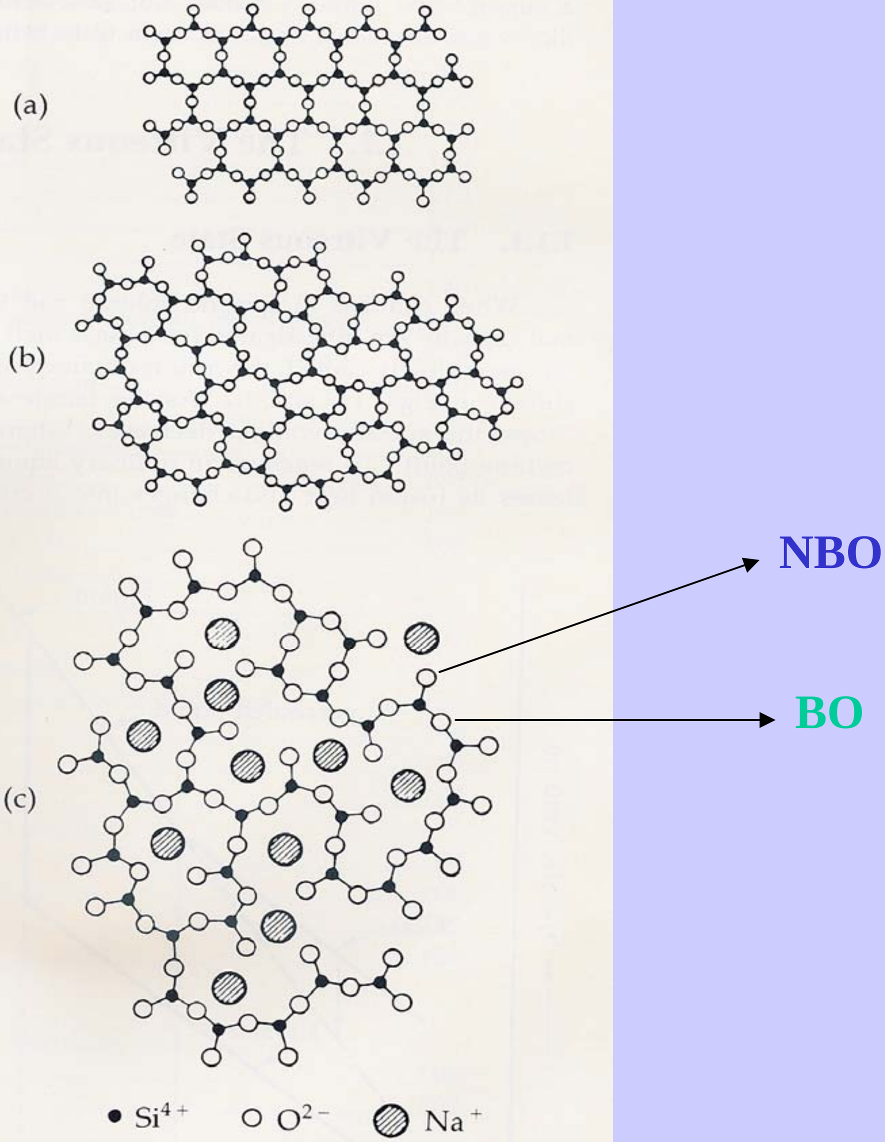
- some other models of glass structure (e.g., the *crystallite* model of Lebedev) actually oppose the idea of a CRN.

## Strong points of Zachariasen's model

- predicts the existence of the main oxide **glass formers** ($SiO_2$, $GeO_2$, $B_2O_3$, $P_2O_5$, …) and **glass modifiers** ($Na_2O$, CaO, …); suggests the existence of bridging oxygen (**BO**) and non-bridging oxygen (**NBO**) species.

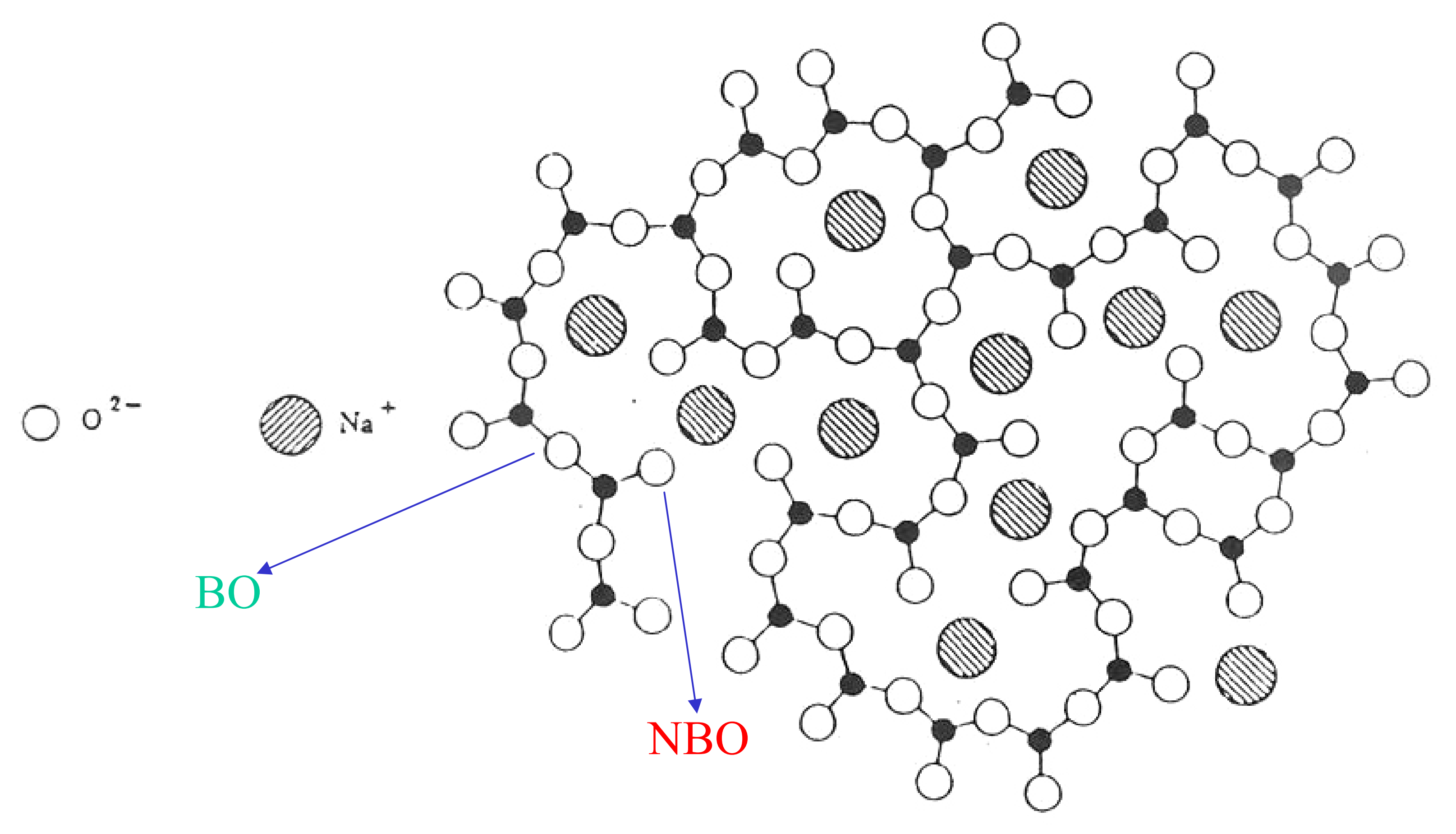
The bottom figure (c) depicts the structure of a $SiO_2$-$Na_2O$ glass, where **BO** and **NBO** species can be identified.

(Adapted from: *Optical glass*, T.S. Izumitani, Hoya Corporation, 1986)



**Network structure of $SiO_4^{4+}$ tetrahedrons: (a) quartz crystal, (b) quartz glass, (c) sodium silicate glass (Ref. 5).**

This figure also depicts the structure of a $SiO_2$-$Na_2O$ glass, where **BO** and **NBO** species can be identified:



## B) **K.H. Sun**'s criterion:

- Establishes a correlation between **glass forming tendency** and chemical **bond strength** in the glass.

*Dissociation energy* of oxides into gaseous elements:

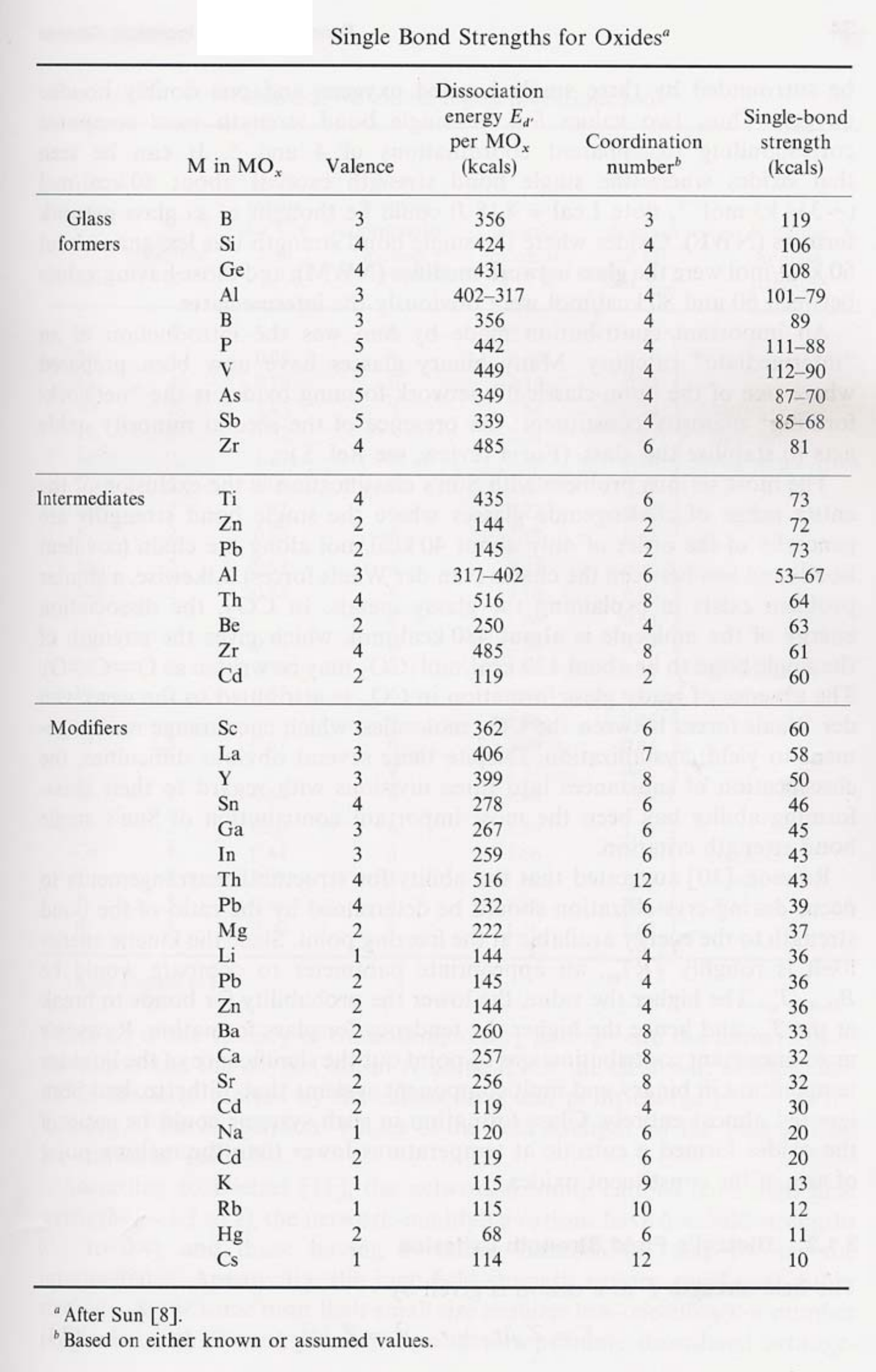
$$E_d^{MOx} = | 1/m\ \Delta H^o{}_f\ (M_mO_n, c) - \Delta H^o{}_f\ (M, g) - n/m\ \Delta H^o{}_f\ (O, g) |$$

$E_d$ refers to a mol of M in $MO_{n/m}$.

$E_b = E_d / CN$ is called the **single bond strength**

The basic idea behind this model is that, when a melt is quenched to form a glass, the stronger the M-O bonds, the more difficult are the structural rearrangements necessary for crystallization and, hence, the easier is glass formation.

(Adapted from: *Fundamentals of inorganic glasses*, A.K. Varshneya, Academic Press, 1994)



Single Bond Strengths for Oxides[a]

| | M in $MO_x$ | Valence | Dissociation energy $E_d$, per $MO_x$ (kcals) | Coordination number[b] | Single-bond strength (kcals) |
|---|---|---|---|---|---|
| Glass formers | B | 3 | 356 | 3 | 119 |
| | Si | 4 | 424 | 4 | 106 |
| | Ge | 4 | 431 | 4 | 108 |
| | Al | 3 | 402–317 | 4 | 101–79 |
| | B | 3 | 356 | 4 | 89 |
| | P | 5 | 442 | 4 | 111–88 |
| | V | 5 | 449 | 4 | 112–90 |
| | As | 5 | 349 | 4 | 87–70 |
| | Sb | 5 | 339 | 4 | 85–68 |
| | Zr | 4 | 485 | 6 | 81 |
| Intermediates | Ti | 4 | 435 | 6 | 73 |
| | Zn | 2 | 144 | 2 | 72 |
| | Pb | 2 | 145 | 2 | 73 |
| | Al | 3 | 317–402 | 6 | 53–67 |
| | Th | 4 | 516 | 8 | 64 |
| | Be | 2 | 250 | 4 | 63 |
| | Zr | 4 | 485 | 8 | 61 |
| | Cd | 2 | 119 | 2 | 60 |
| Modifiers | Sc | 3 | 362 | 6 | 60 |
| | La | 3 | 406 | 7 | 58 |
| | Y | 3 | 399 | 8 | 50 |
| | Sn | 4 | 278 | 6 | 46 |
| | Ga | 3 | 267 | 6 | 45 |
| | In | 3 | 259 | 6 | 43 |
| | Th | 4 | 516 | 12 | 43 |
| | Pb | 4 | 232 | 6 | 39 |
| | Mg | 2 | 222 | 6 | 37 |
| | Li | 1 | 144 | 4 | 36 |
| | Pb | 2 | 145 | 4 | 36 |
| | Zn | 2 | 144 | 4 | 36 |
| | Ba | 2 | 260 | 8 | 33 |
| | Ca | 2 | 257 | 8 | 32 |
| | Sr | 2 | 256 | 8 | 32 |
| | Cd | 2 | 119 | 4 | 30 |
| | Na | 1 | 120 | 6 | 20 |
| | Cd | 2 | 119 | 6 | 20 |
| | K | 1 | 115 | 9 | 13 |
| | Rb | 1 | 115 | 10 | 12 |
| | Hg | 2 | 68 | 6 | 11 |
| | Cs | 1 | 114 | 12 | 10 |

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[a] After Sun [8].

[b] Based on either known or assumed values.