UNIVERSITY OF CAMBRIDGE

Ionic conductors

Lecture 8

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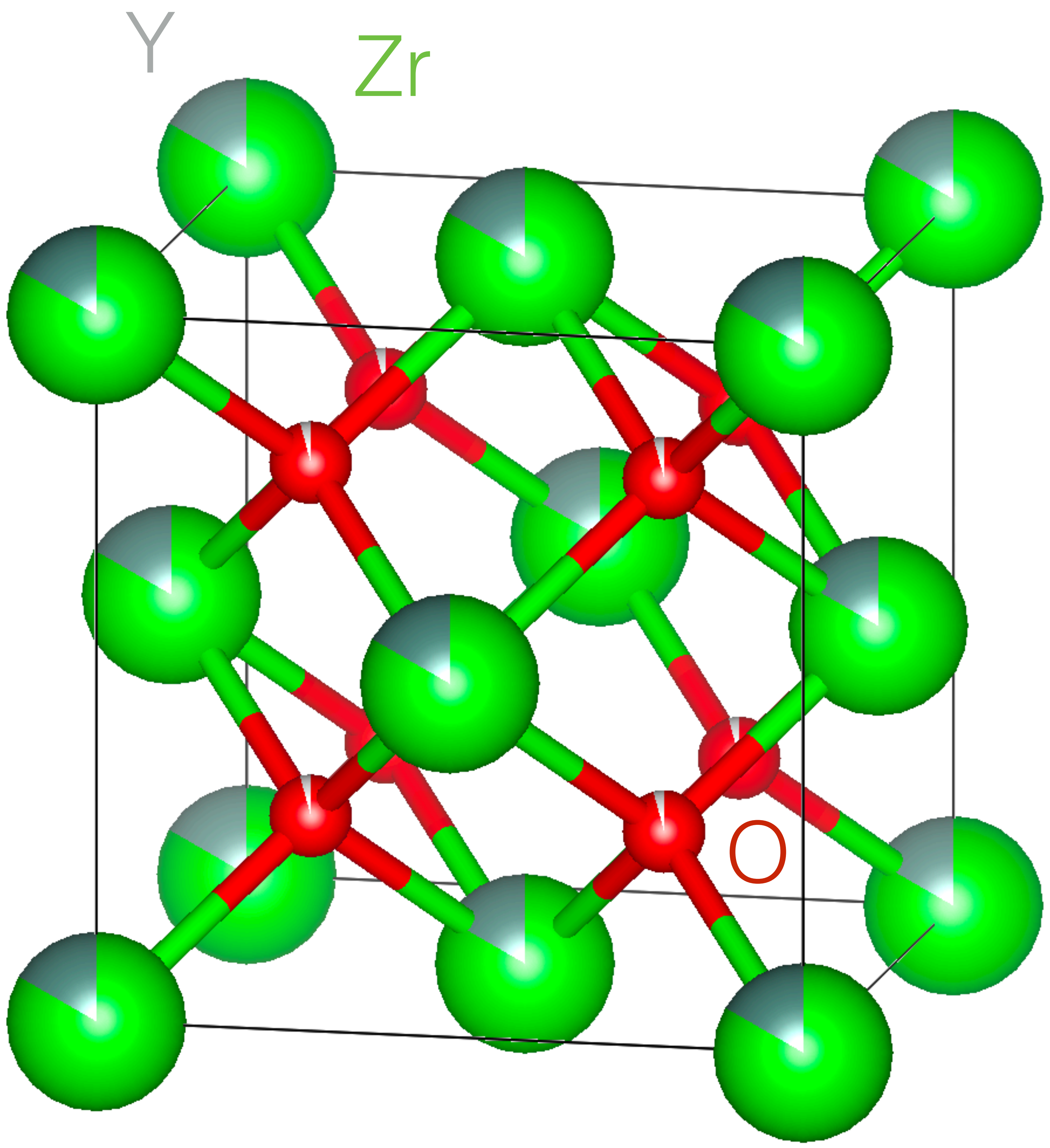
Course B: Materials for Devices

Professor M does Science

http://www.tcm.phy.cam.ac.uk/~bm418/

Ionic conduction



- Yttrium stabilised zirconia
- Complex structure (see Lecture 8)
- No conduction electrons (band gap)

$$\sigma \sim 0.1\ \mathrm{Sm}^{-1}$$
$$\sigma = 0.02\ \mathrm{Sm}^{-1}\ (800\,^{\circ}\mathrm{C})$$

- Copper (Cu): $\sigma = 6.0 \times 10^{7}\ \mathrm{Sm}^{-1}$
- Al_2O_3: $\sigma = 10^{-10}\ \mathrm{Sm}^{-1}$

Fick's equation with drift current

$$\boxed{j_x = -qD\frac{\partial n}{\partial x} - \sigma\frac{\partial V}{\partial x}}$$

- Continuum theory of ionic conduction
- Diffusion current caused by concentration gradients
- Drift current caused by applied field

Nernst-Einstein equation

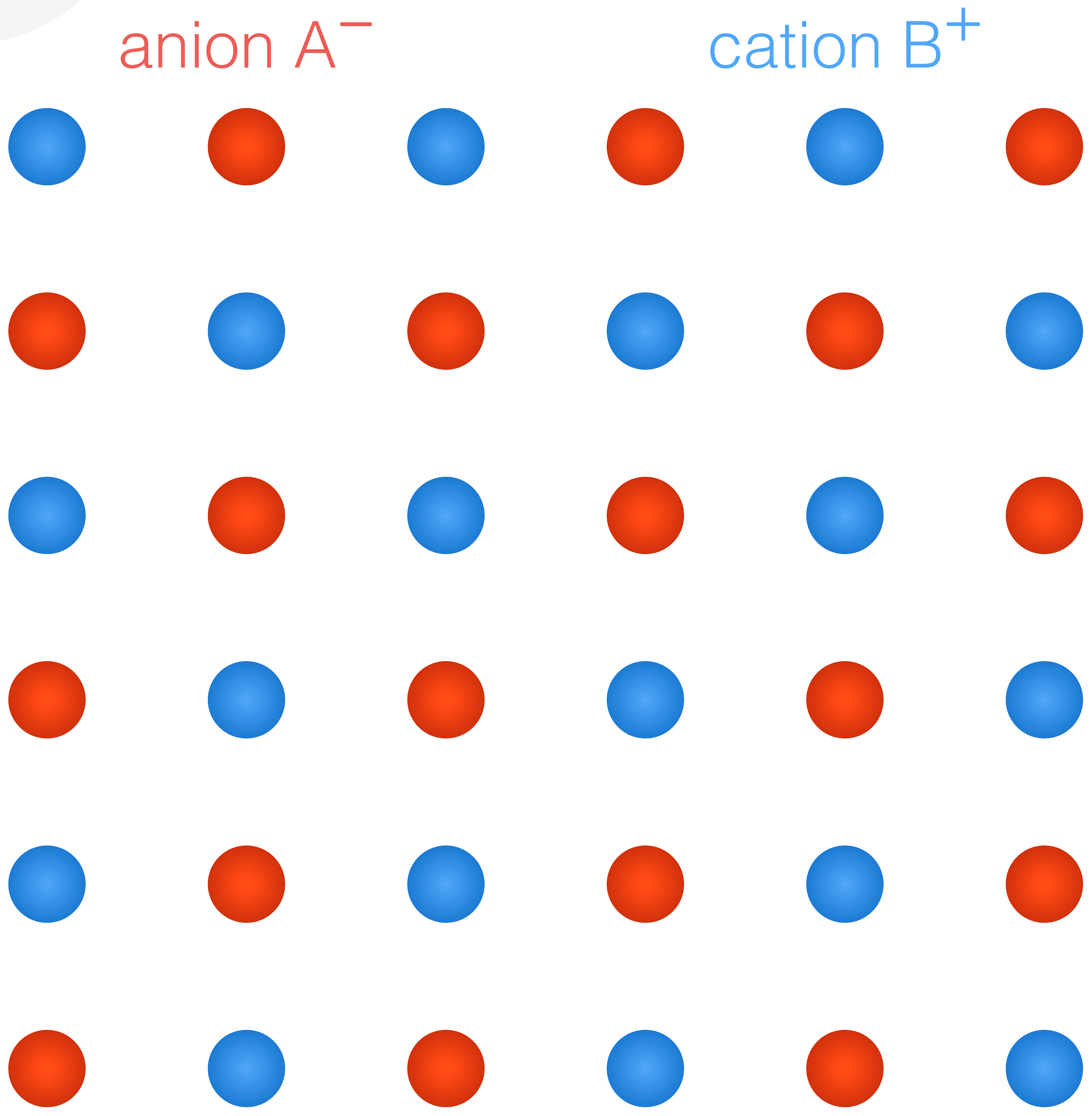
$$\boxed{\frac{\sigma}{D} = \frac{nq^2}{k_\mathrm{B}T}}$$

- Steady state: diffusion and drift currents balance
- Mathematical relationship between conductivity σ and diffusivity D

Defects in materials: point defects

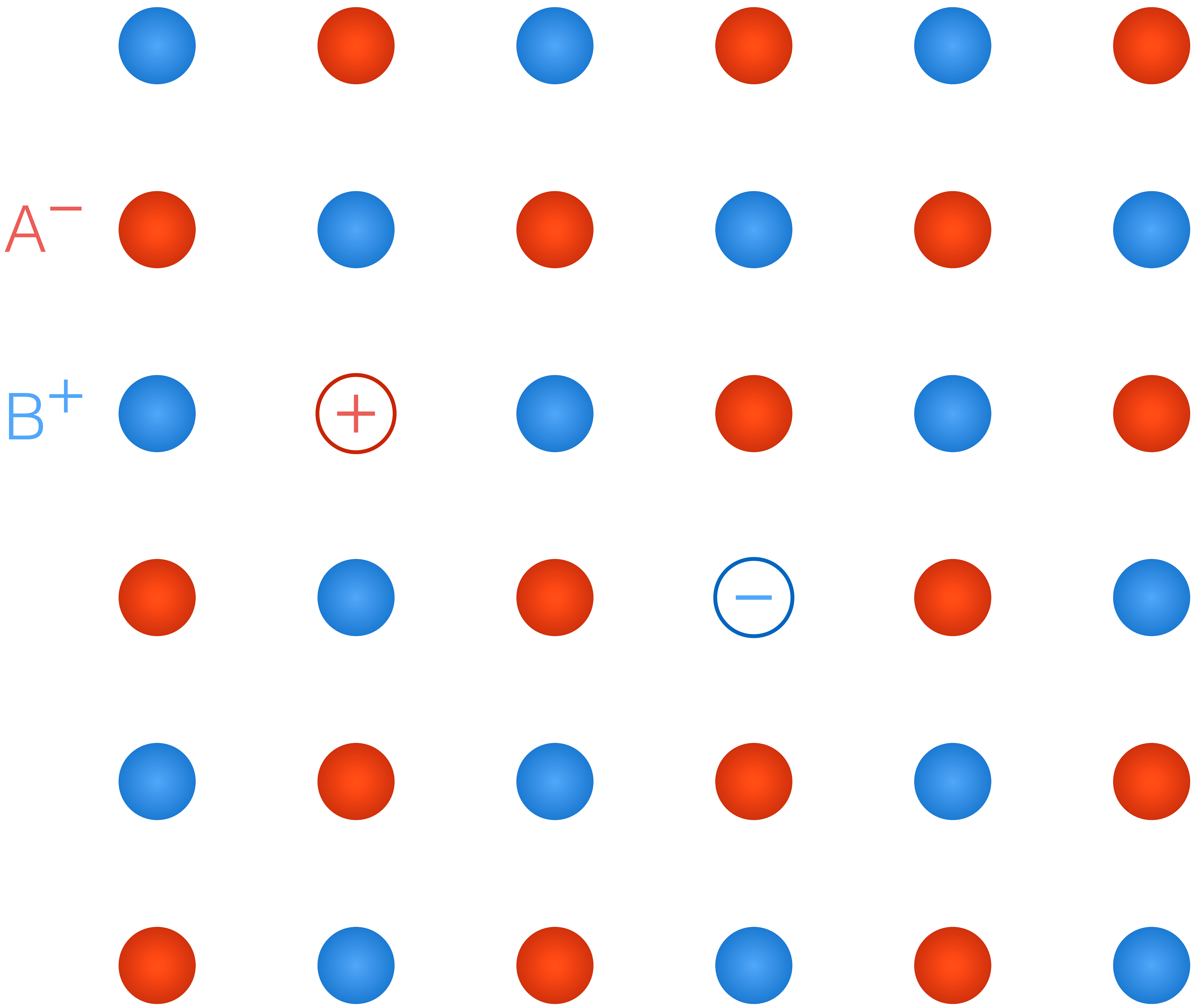
- Vacancy defects: one atom is missing
- Interstitial defects: one extra atom in the lattice
- Substitutional defect: replacing one atom by another atom
- Antisite defect: exchanging the positions of two atoms
- Topological defects: local changes in bonding…
- …

Defects in materials



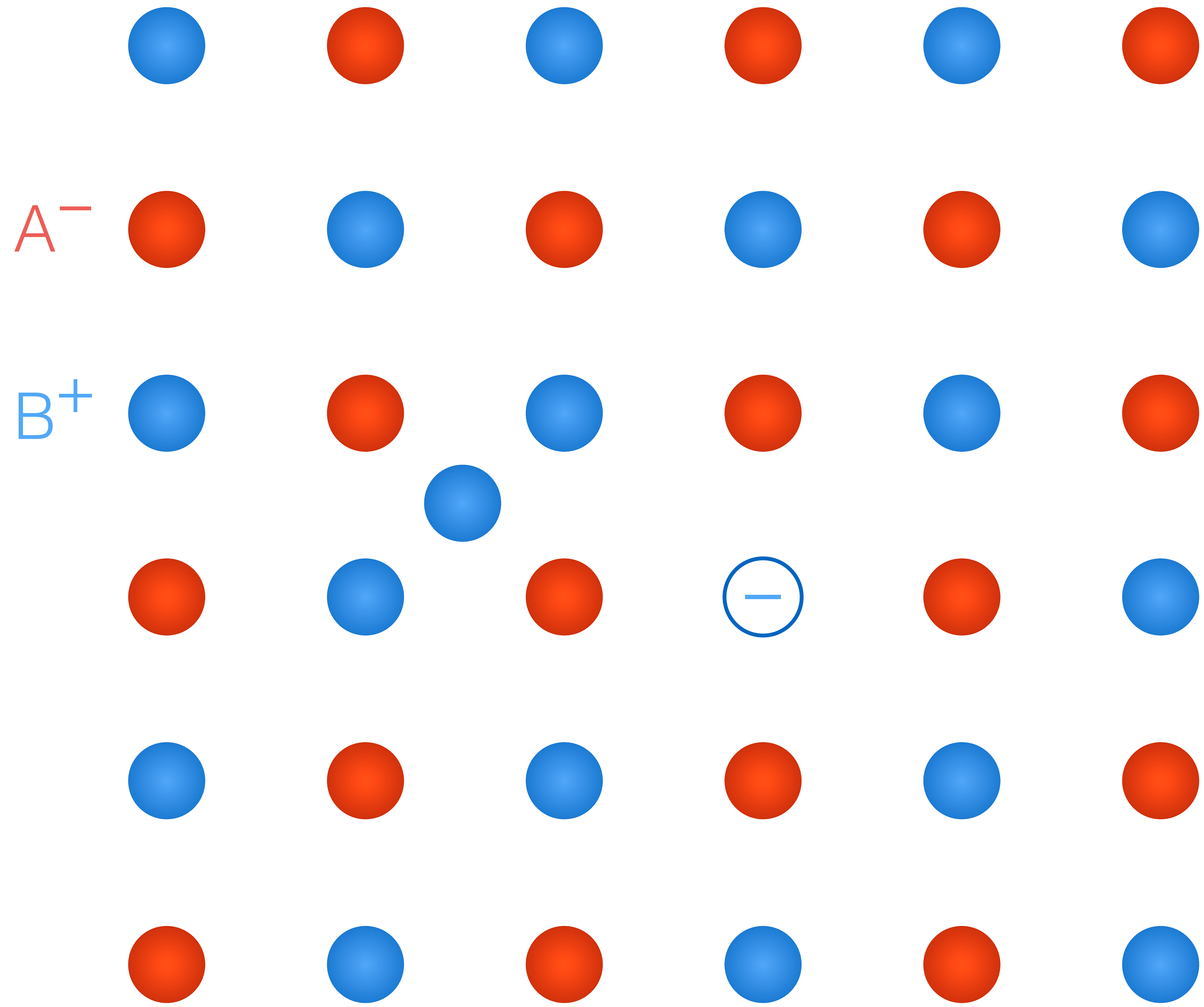
- Ionic crystal: A^-B^+

Defects in materials: Schottky defect



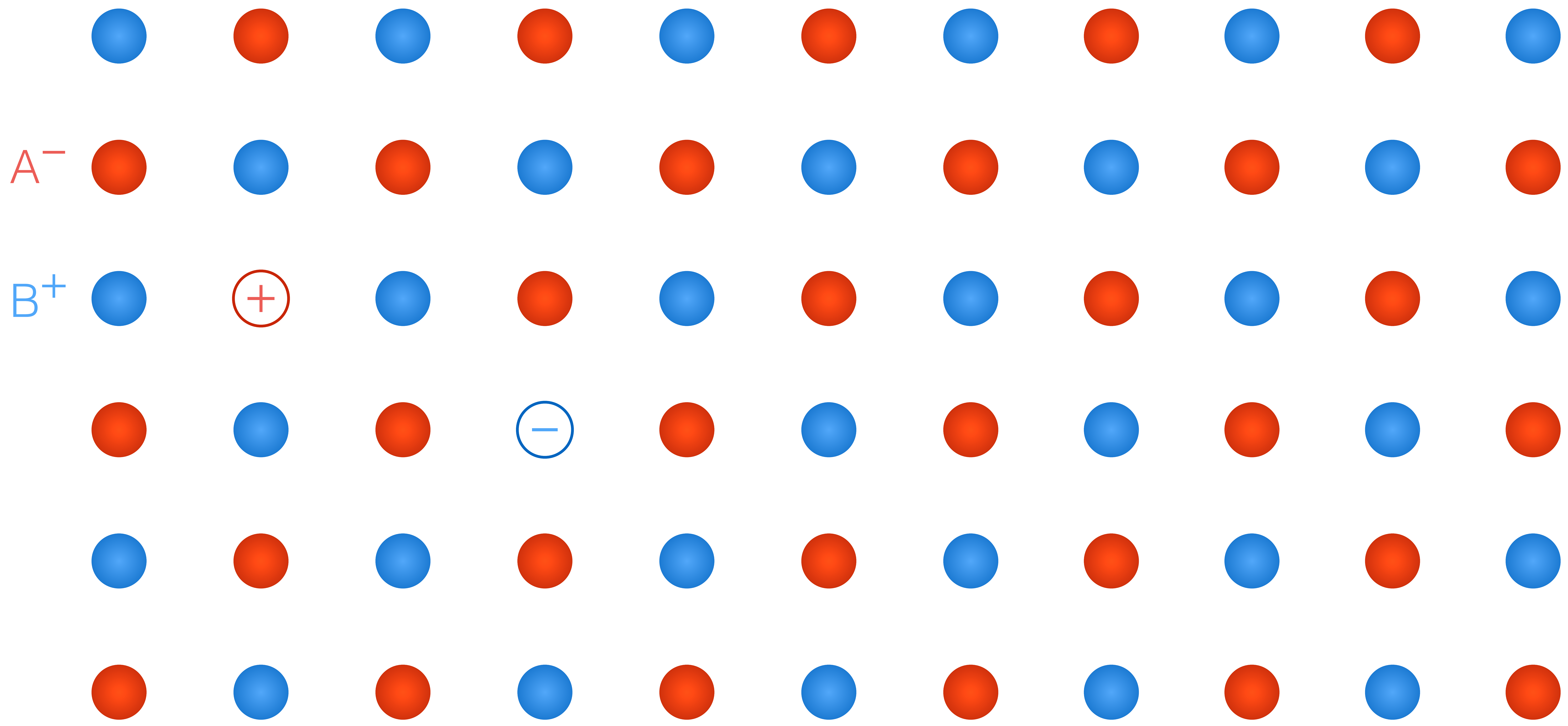
- Ionic crystal: A^-B^+
- Stoichiometric defect:
  - One A^- vacancy
  - One B^+ vacancy
- NaCl, cubic ZrO_2

Defects in materials: Frenkel defect

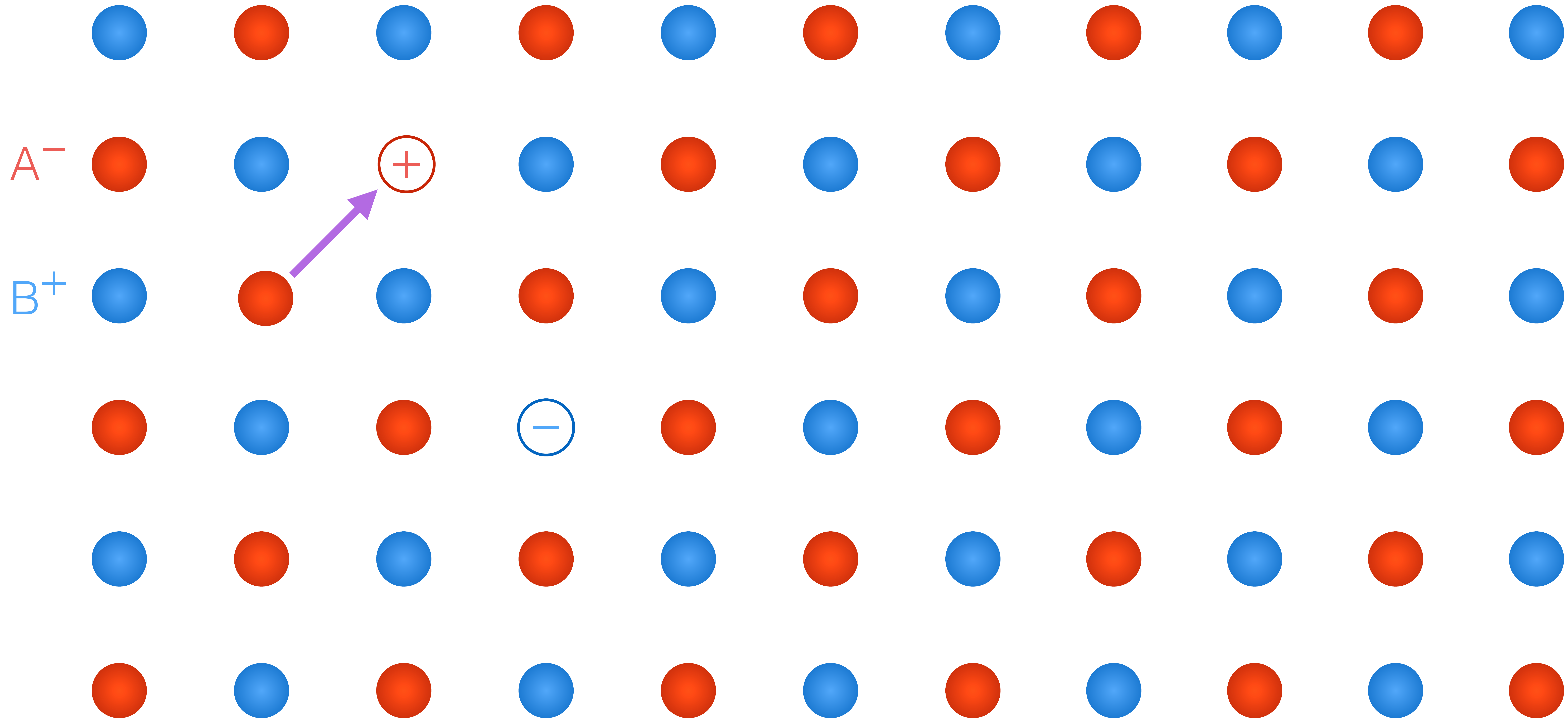


- Ionic crystal: A^-B^+
- Stoichiometric defect:
  - One B^+ vacancy
  - One B^+ interstitial
- ZnS, AgCl

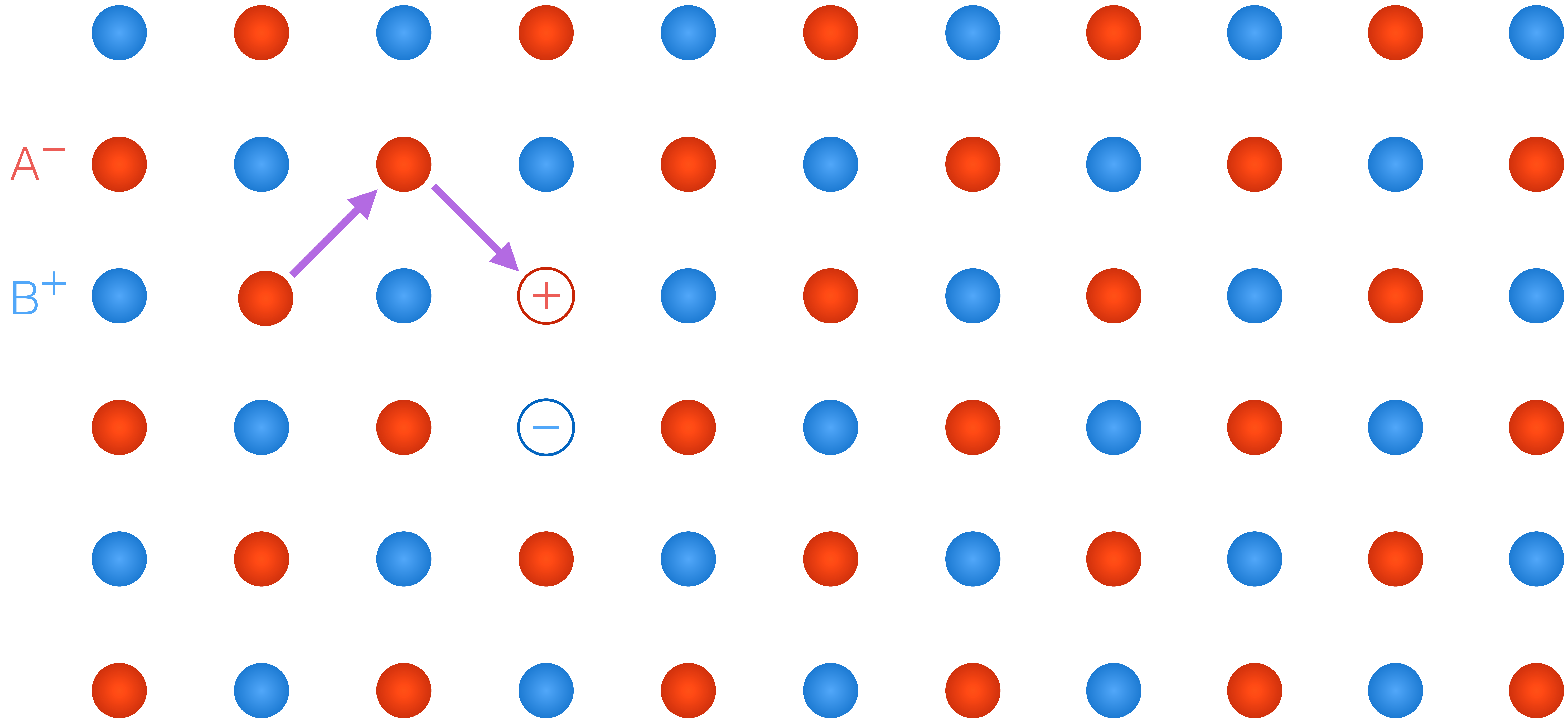
Ionic motion in crystals



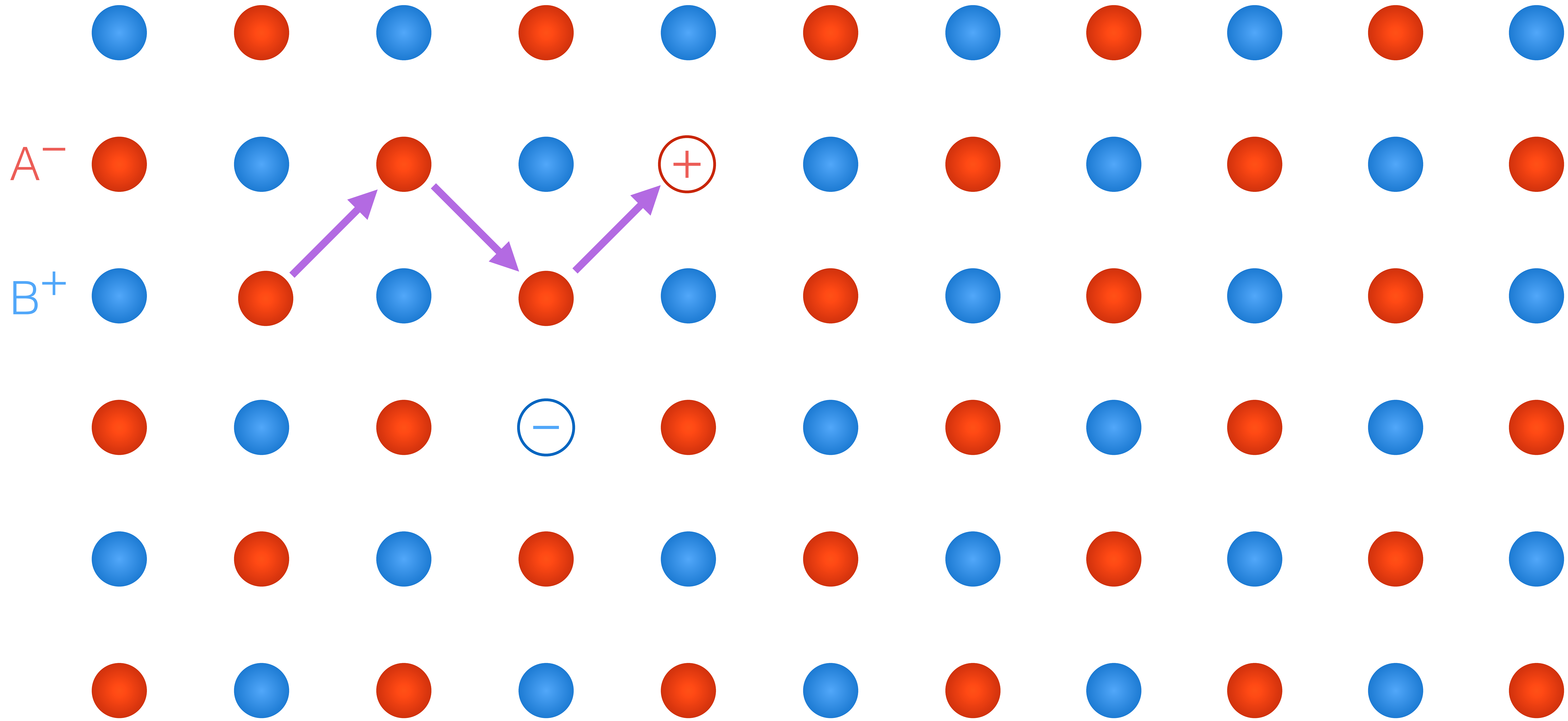
Ionic motion in crystals



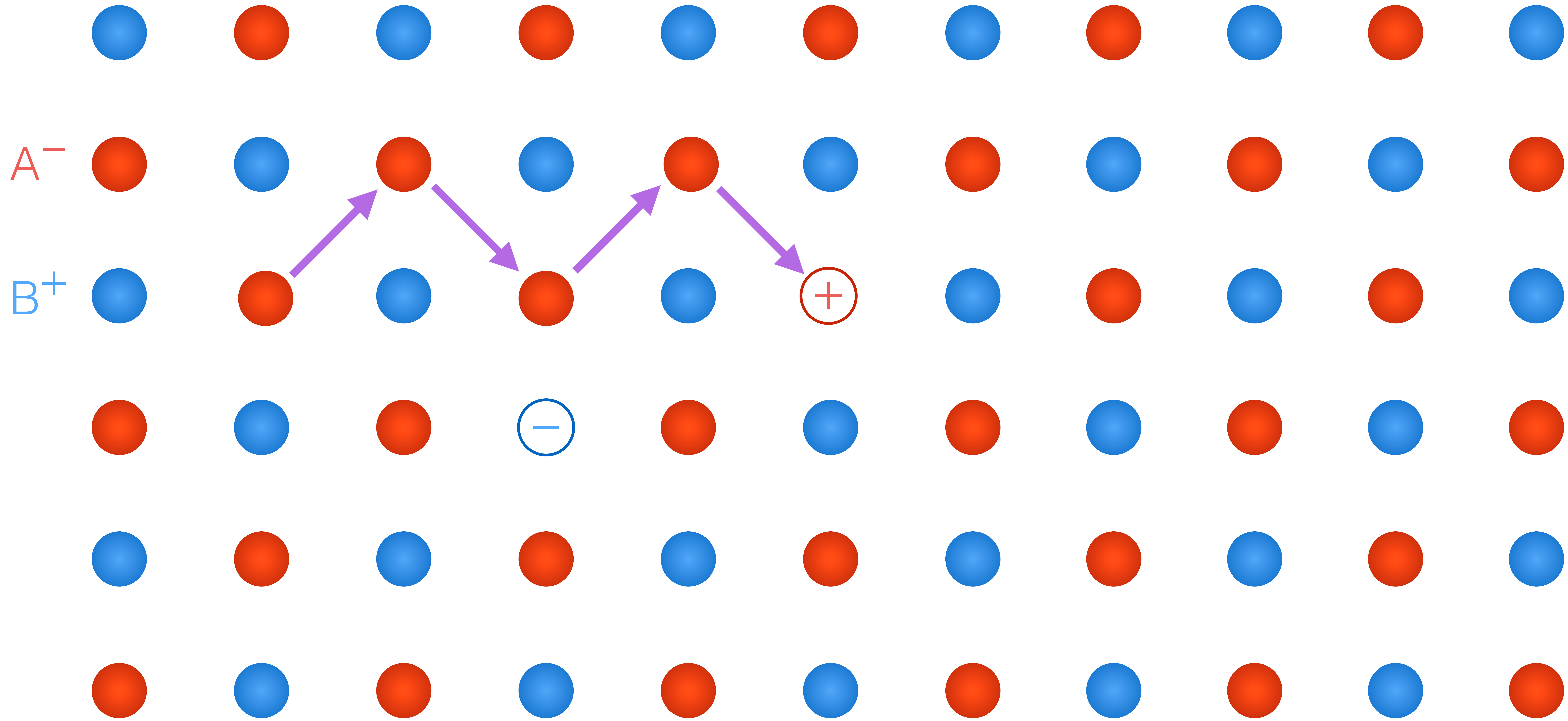
Ionic motion in crystals



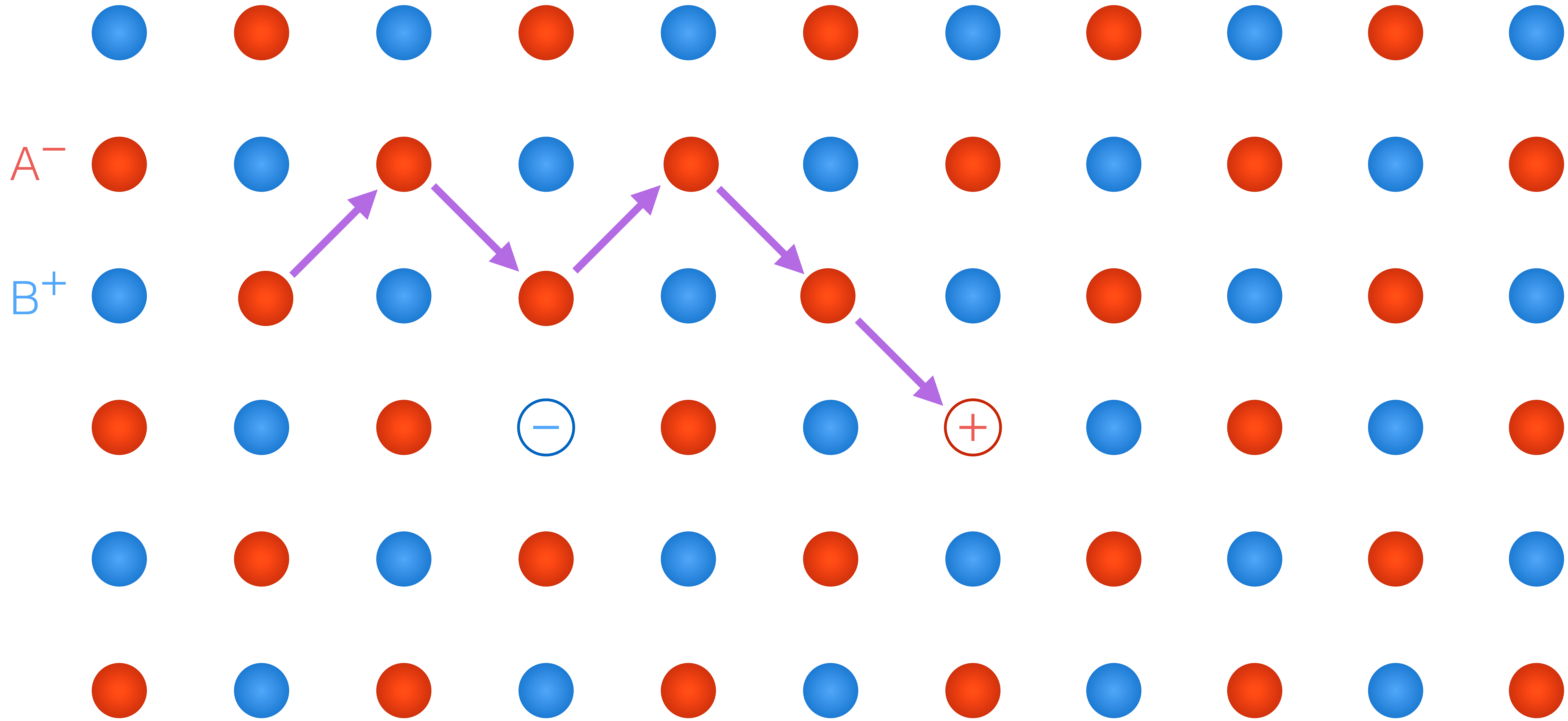
Ionic motion in crystals



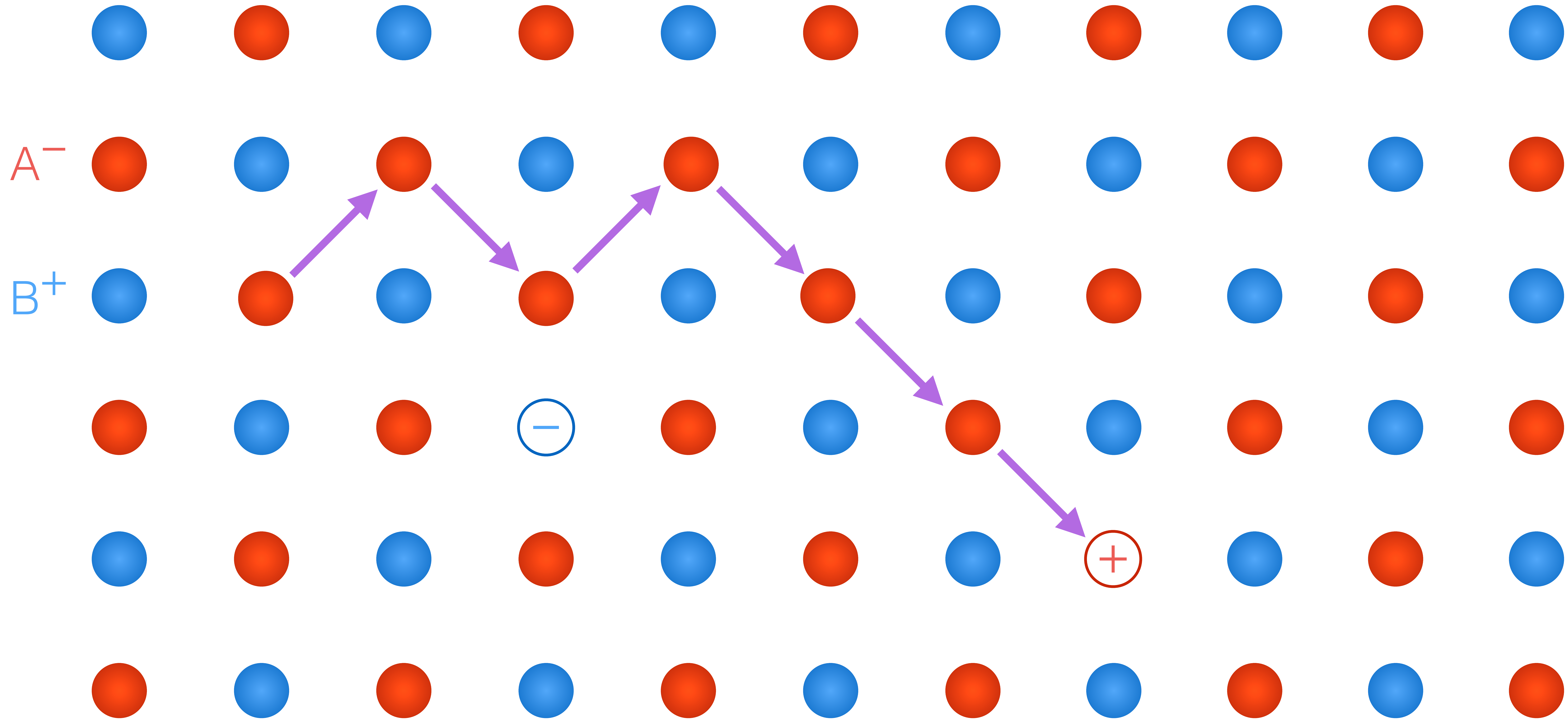
Ionic motion in crystals



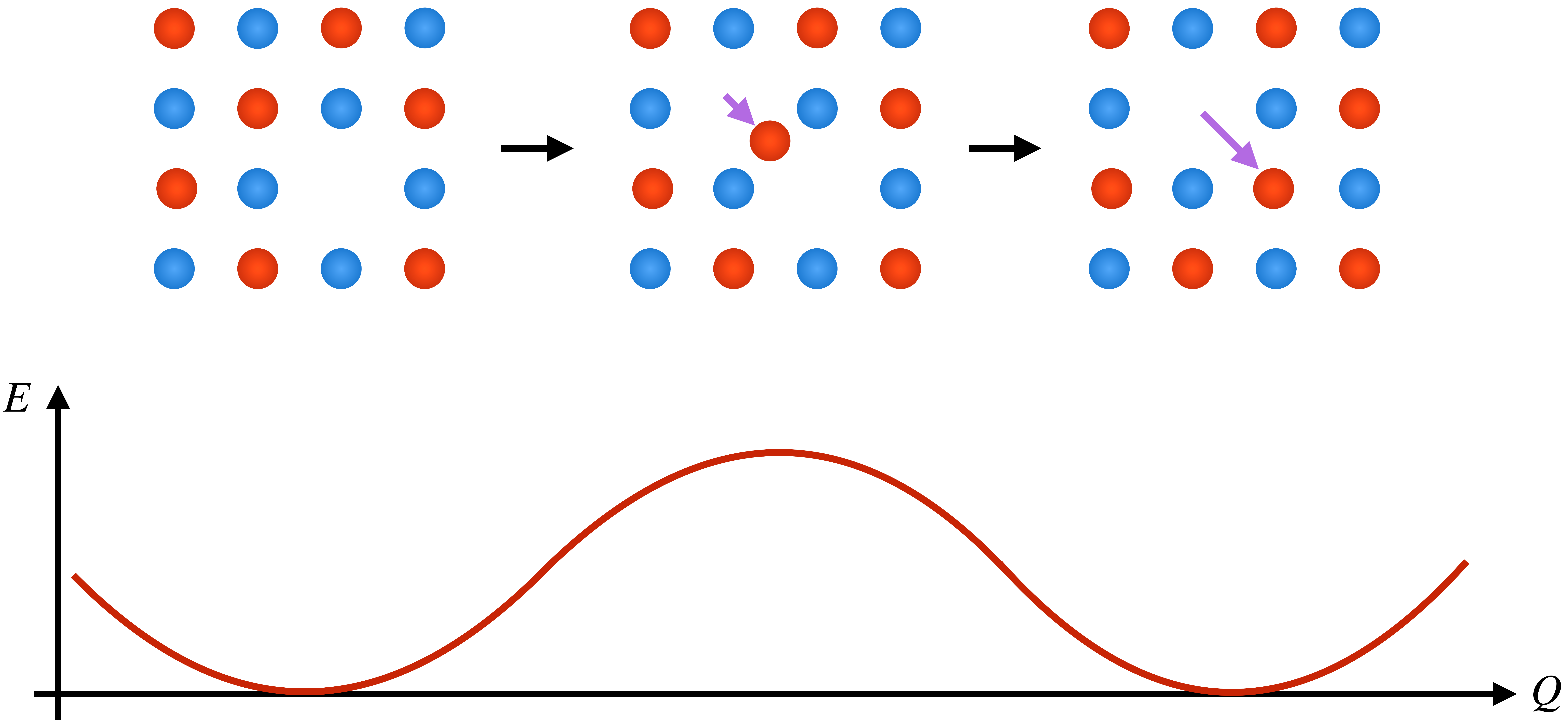
Ionic motion in crystals



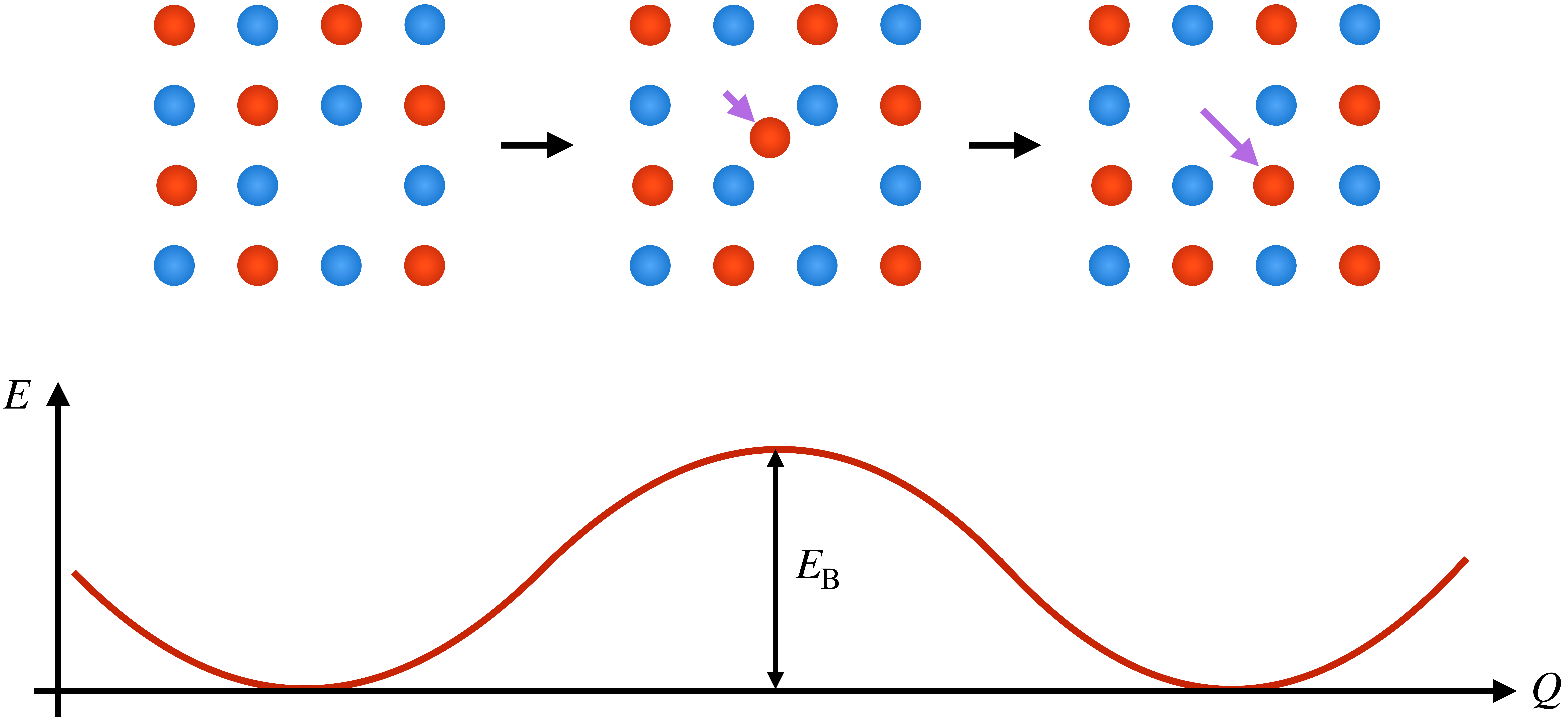
Ionic motion in crystals



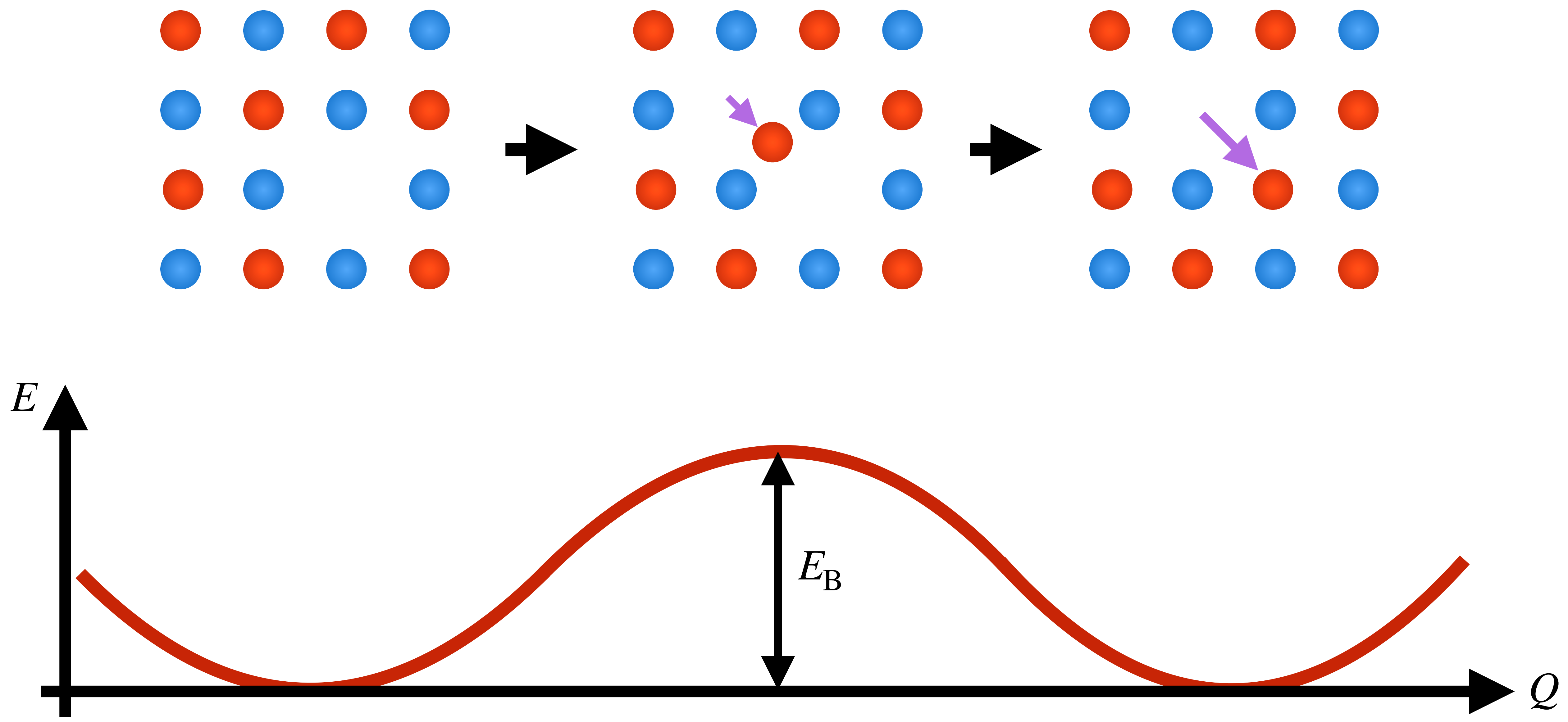
Site jump



Site jump



Arrhenius equation



$$\boxed{D = D_0 e^{-\frac{E_B}{k_B T}}}$$

D : diffusivity $[\mathrm{m^2 s^{-1}}]$

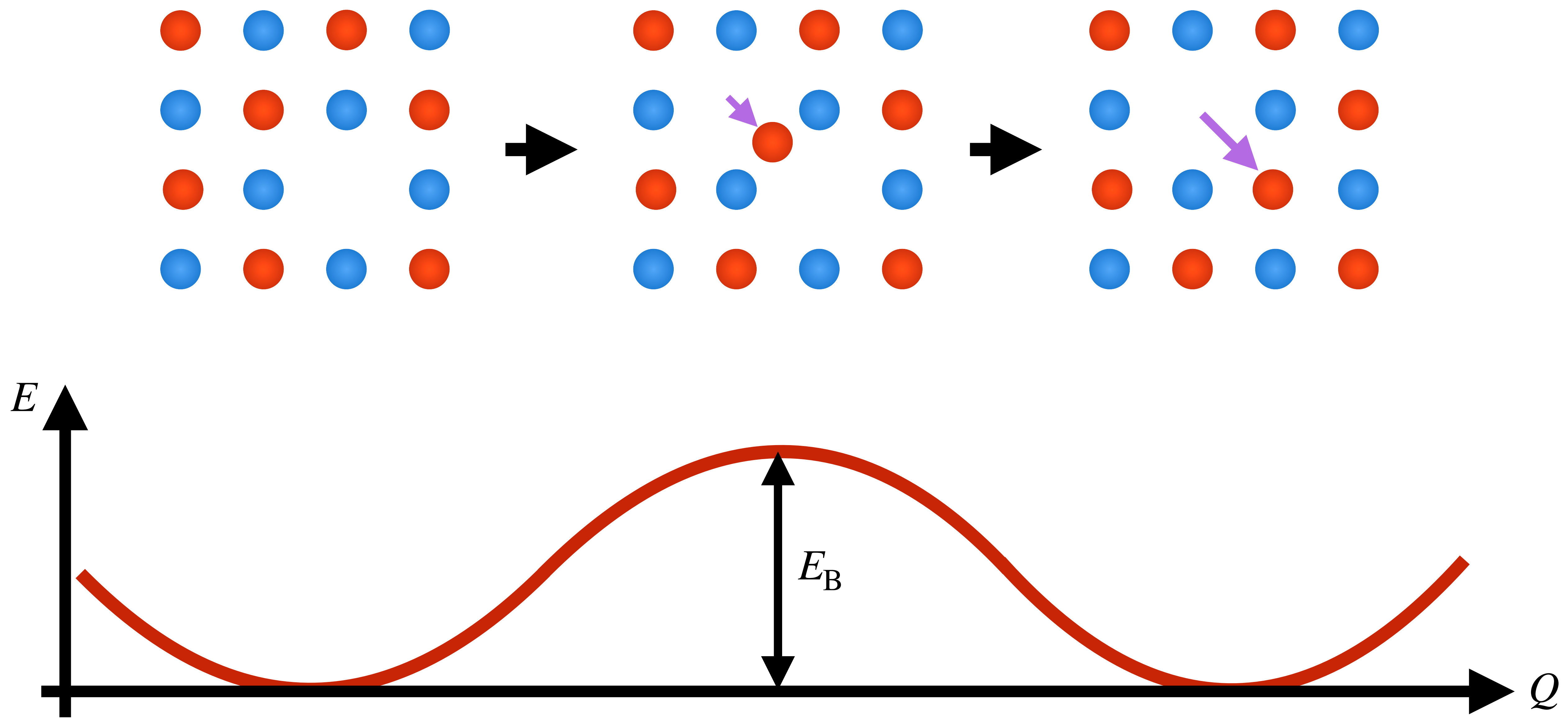
D_0 : pre-exponential factor $[\mathrm{m^2 s^{-1}}]$

E_B : energy barrier $[\mathrm{J}]$

k_B : Boltzmann constant $[1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}}]$

T : temperature $[\mathrm{K}]$

Arrhenius equation



$$\boxed{D = D_0 e^{-\frac{E_B}{k_B T}}}$$

$$D_0 \sim a^2 \Gamma$$

D_0 : pre-exponential factor $[m^2 s^{-1}]$

a : jump distance $[m]$

Γ : jump rate $[s^{-1}]$

Arrhenius plots

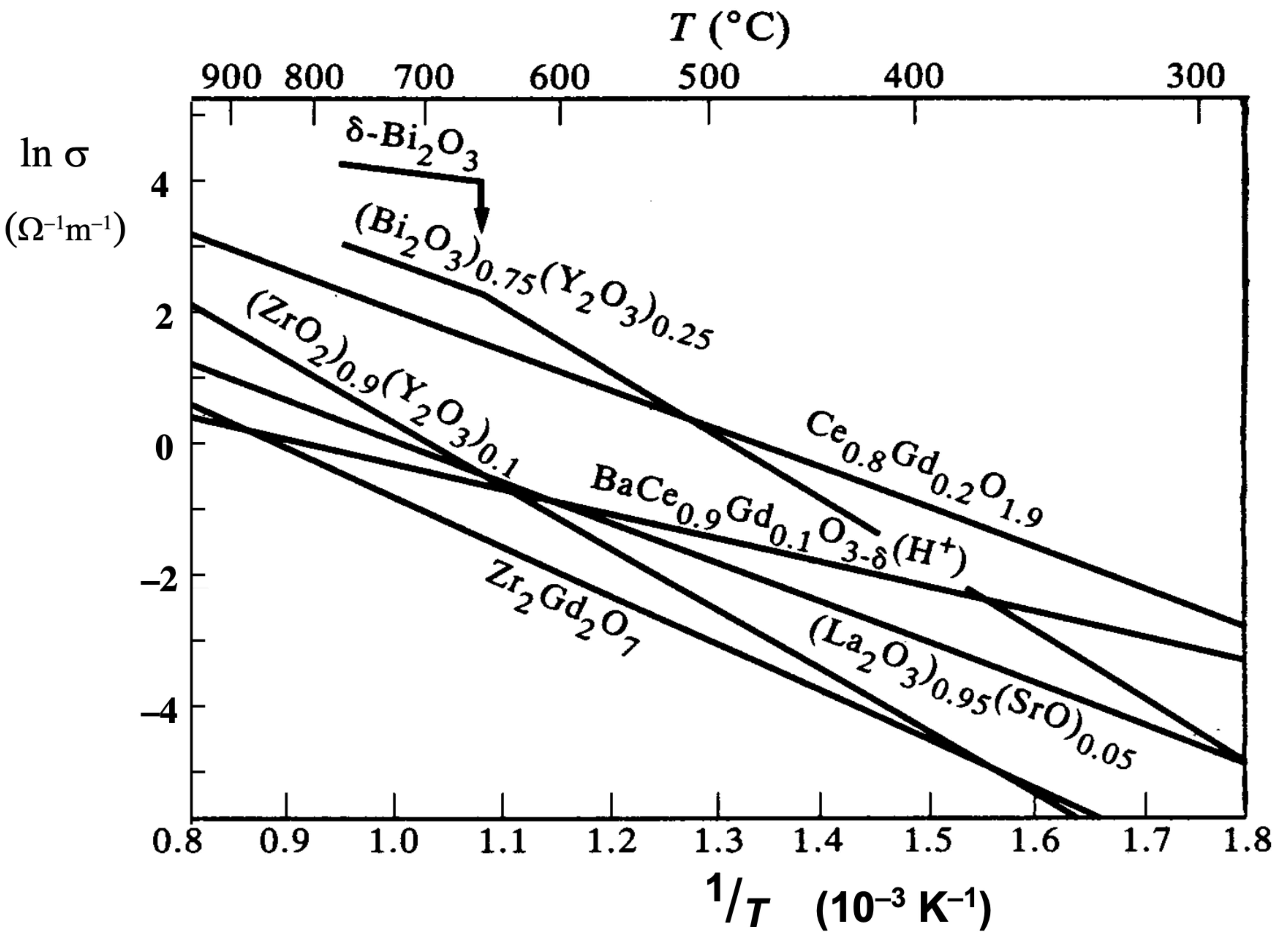
- *See derivation Arrhenius relation*

$$\boxed{\ln \sigma = \ln \sigma_0 - \left(\frac{E_B}{k_B}\right)\frac{1}{T}} \qquad \sigma_0 = \frac{D_0 n_0 q^2}{k_B T}$$

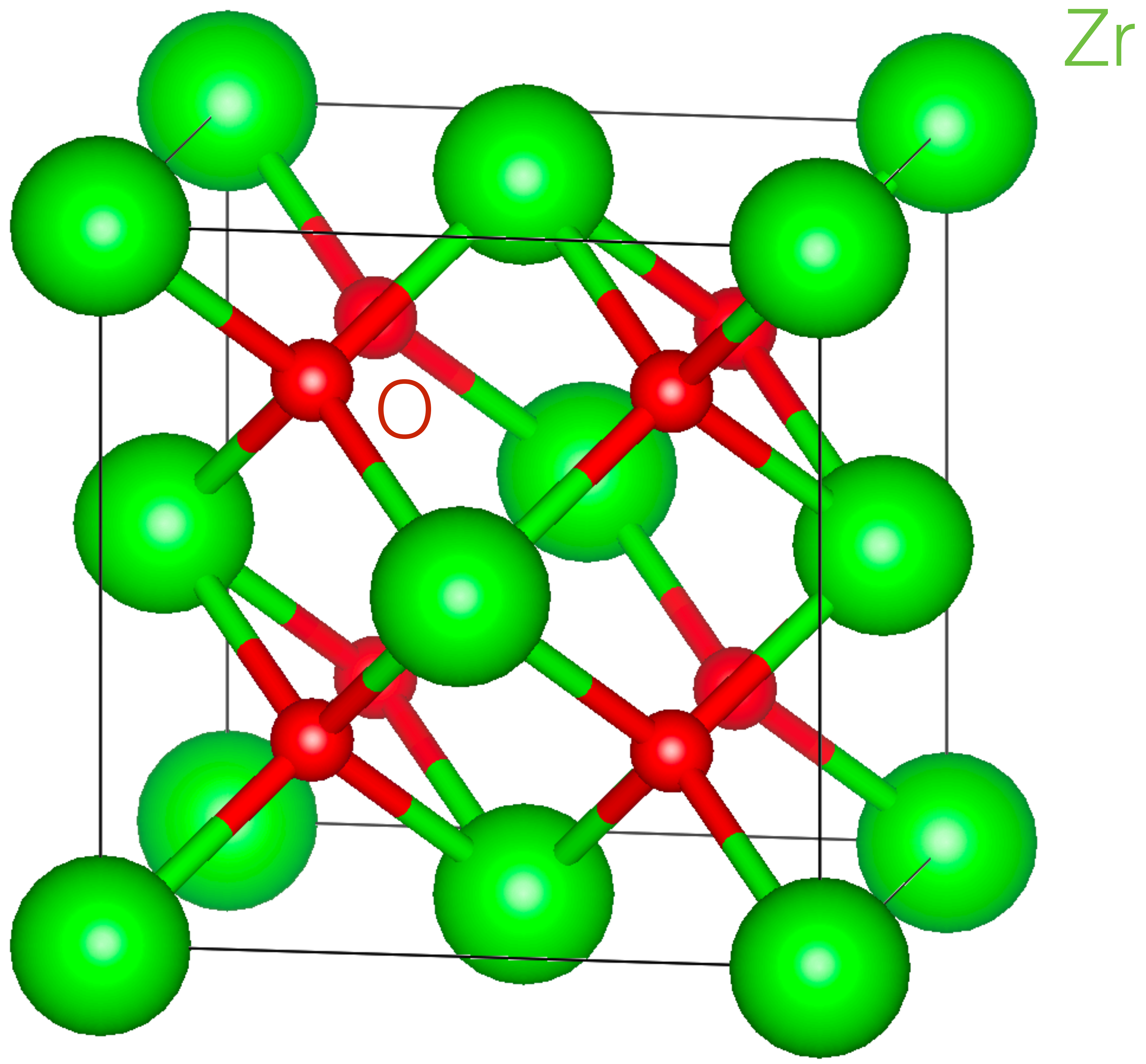
Arrhenius plots

$$\boxed{\ln\sigma = \ln\sigma_0 - \left(\frac{E_B}{k_B}\right)\frac{1}{T}}$$

$$\sigma_0 = \frac{D_0 n_0 q^2}{k_B T}$$



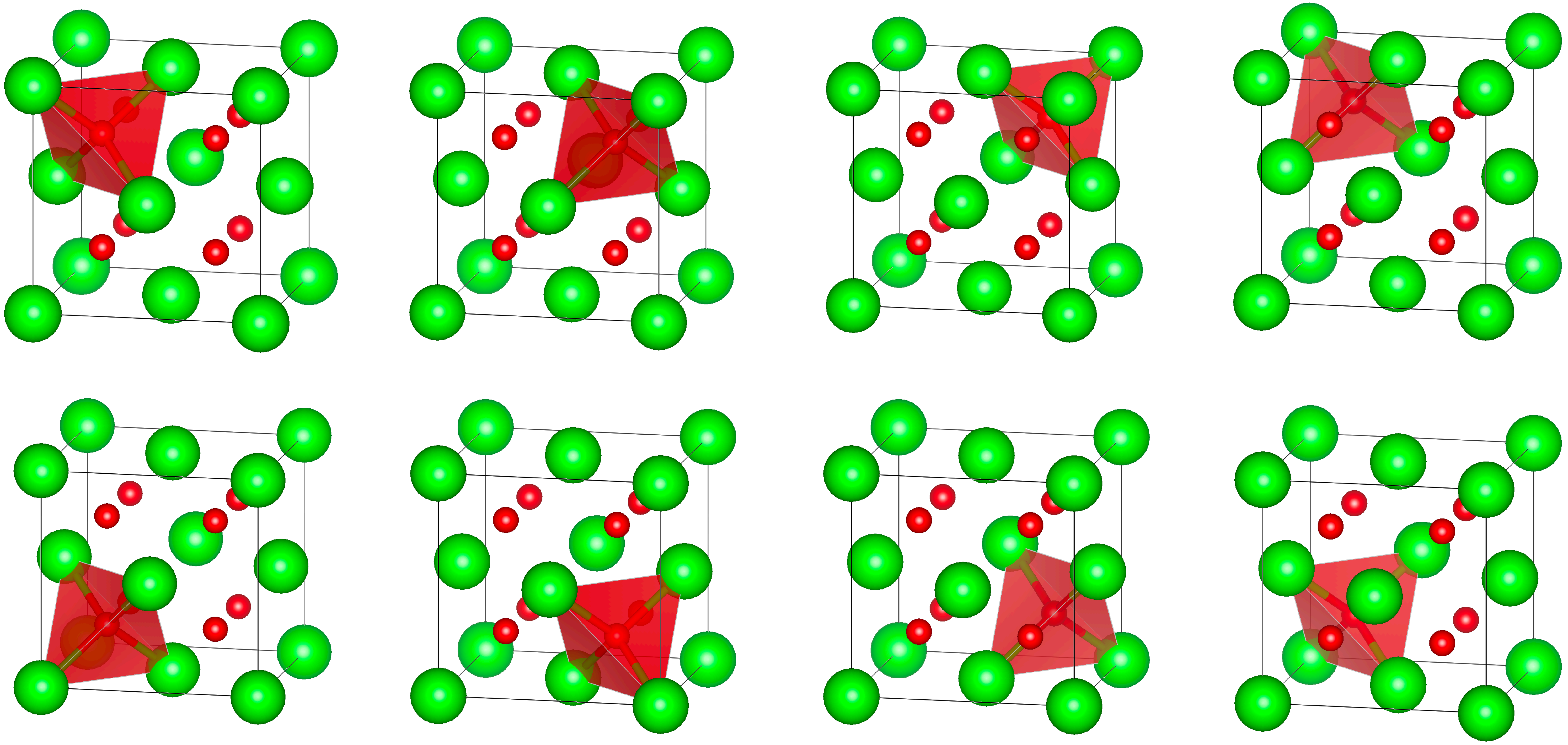
Zirconium dioxide ZrO_2 (zirconia)



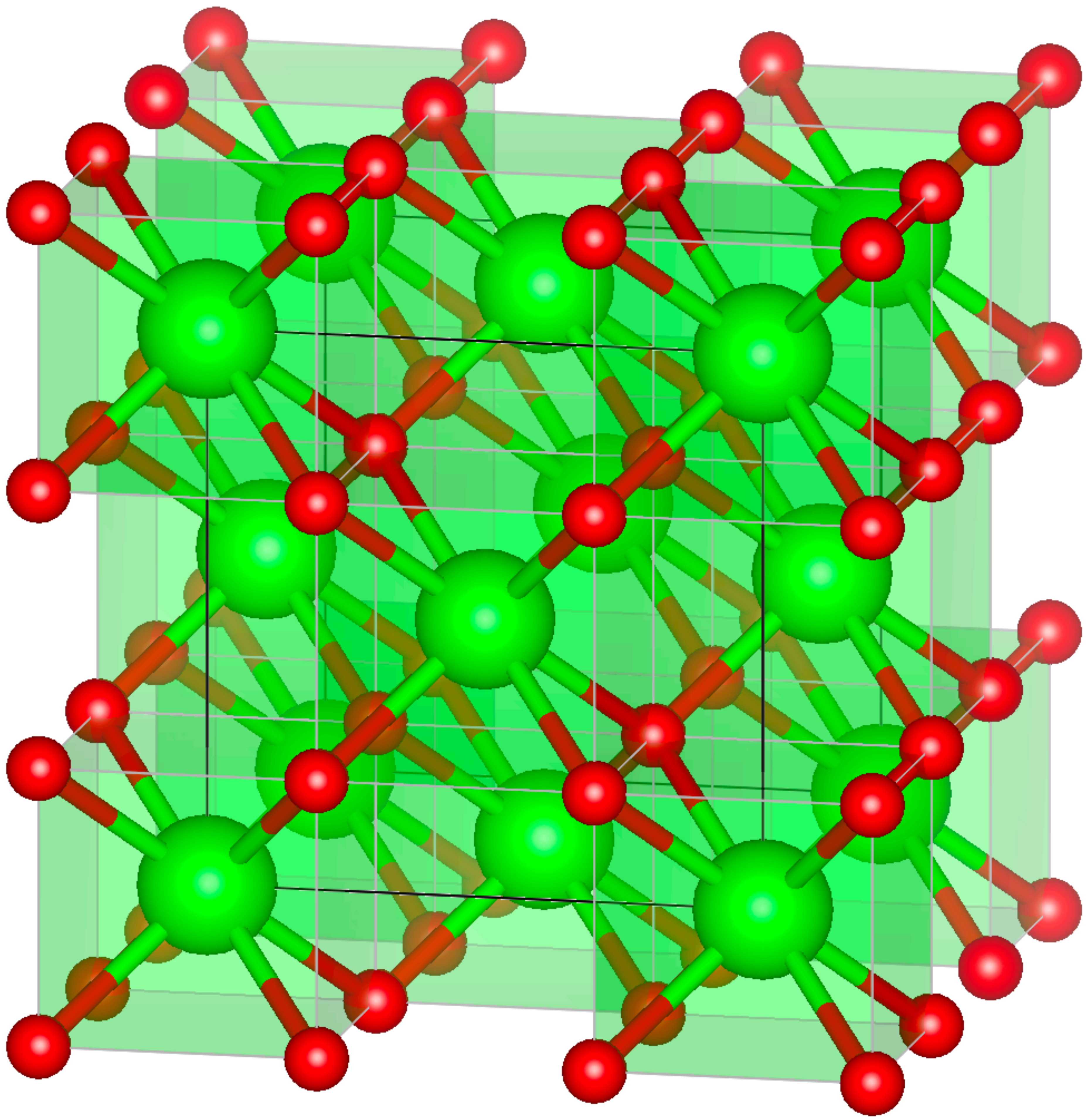
- Zr sublattice is fcc
- 8 tetrahedral interstices occupied by O
- Fluorite structure (Course A)

Zirconium dioxide ZrO_2 (zirconia)

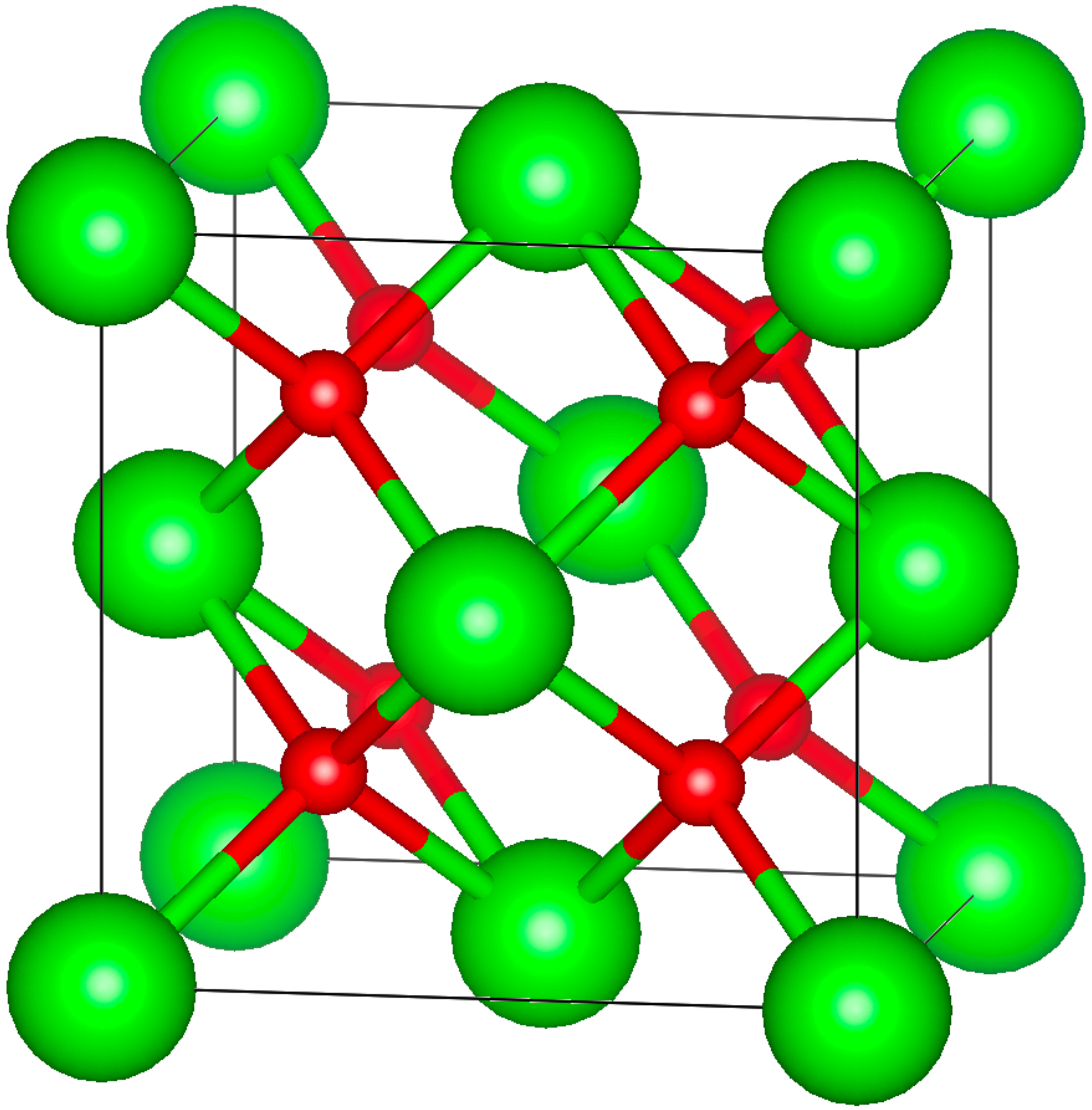
tetrahedral interstice



Zirconium dioxide ZrO_2 (zirconia)



Zirconium dioxide ZrO_2 (zirconia)



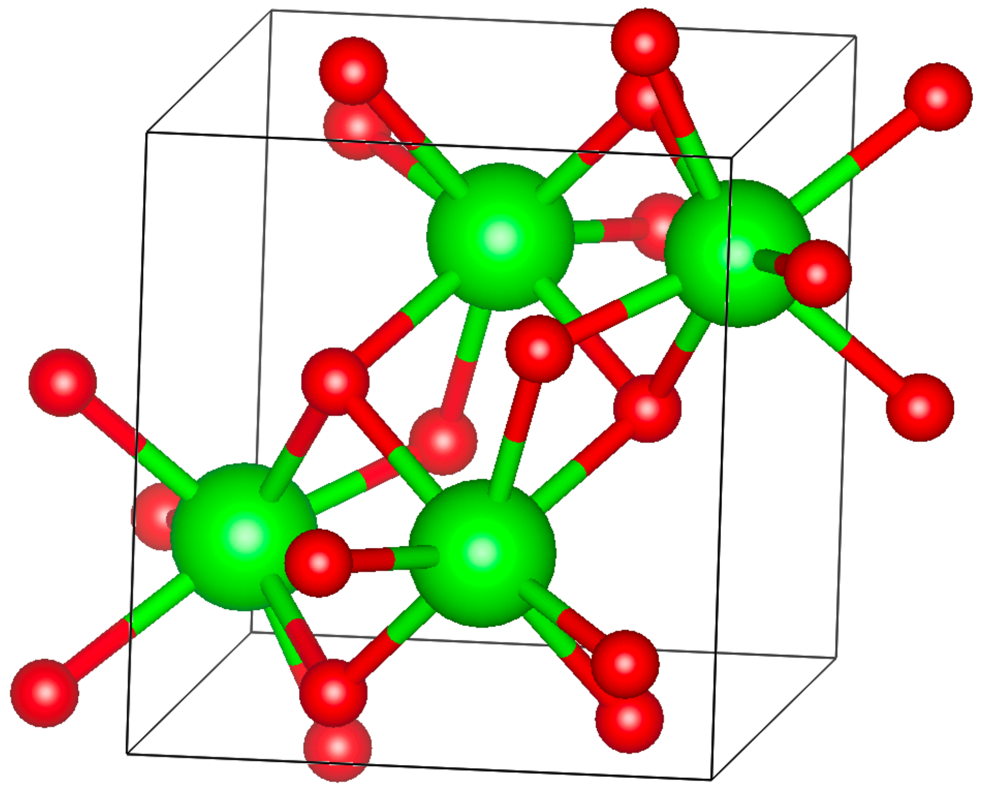
$8\ O^{2-}$ $4\ Zr^{4+}$

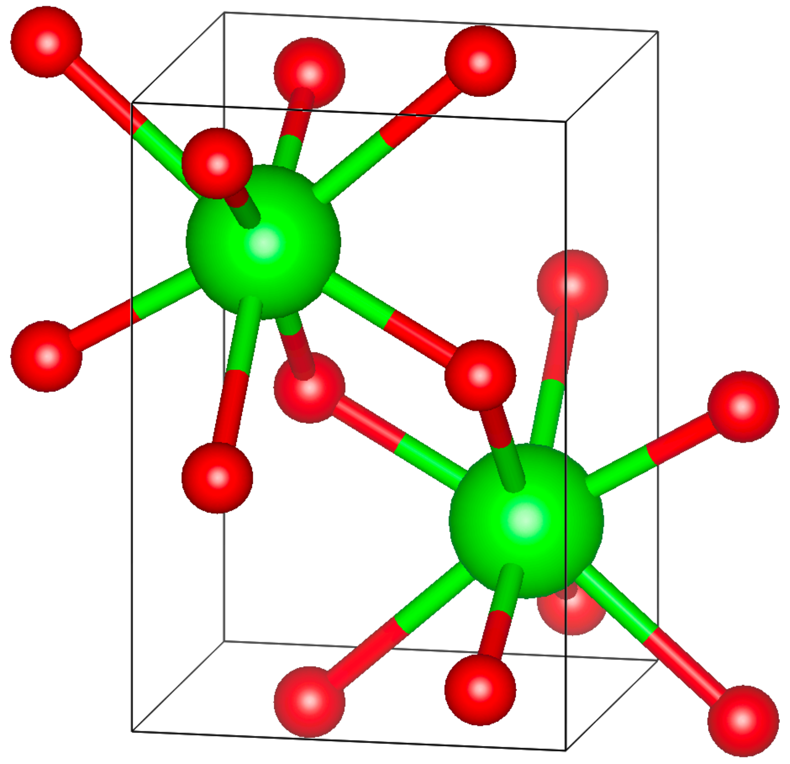
- Charge balance:

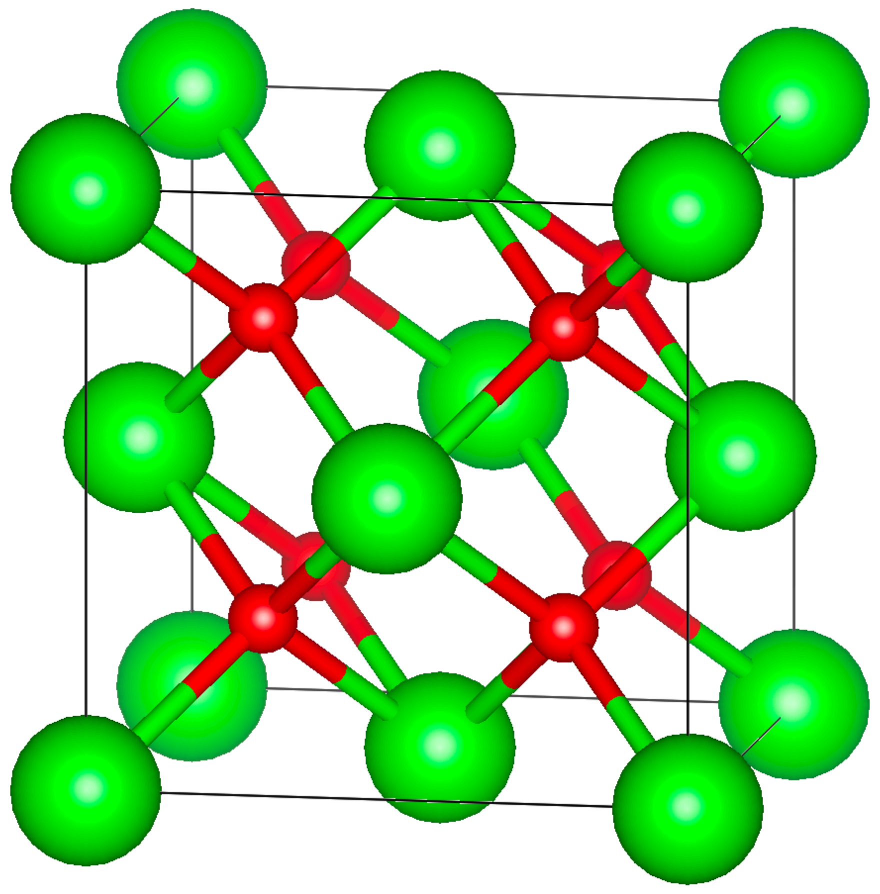
$$8 \times (-2) + 4 \times (+4) = -16 + 16 = 0$$

Phase diagram of ZrO_2

monoclinic	tetragonal	cubic
$a \neq b \neq c$	$a = b \neq c$	$a = b = c$
$\alpha = \beta = 90^\circ \neq \gamma$	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$



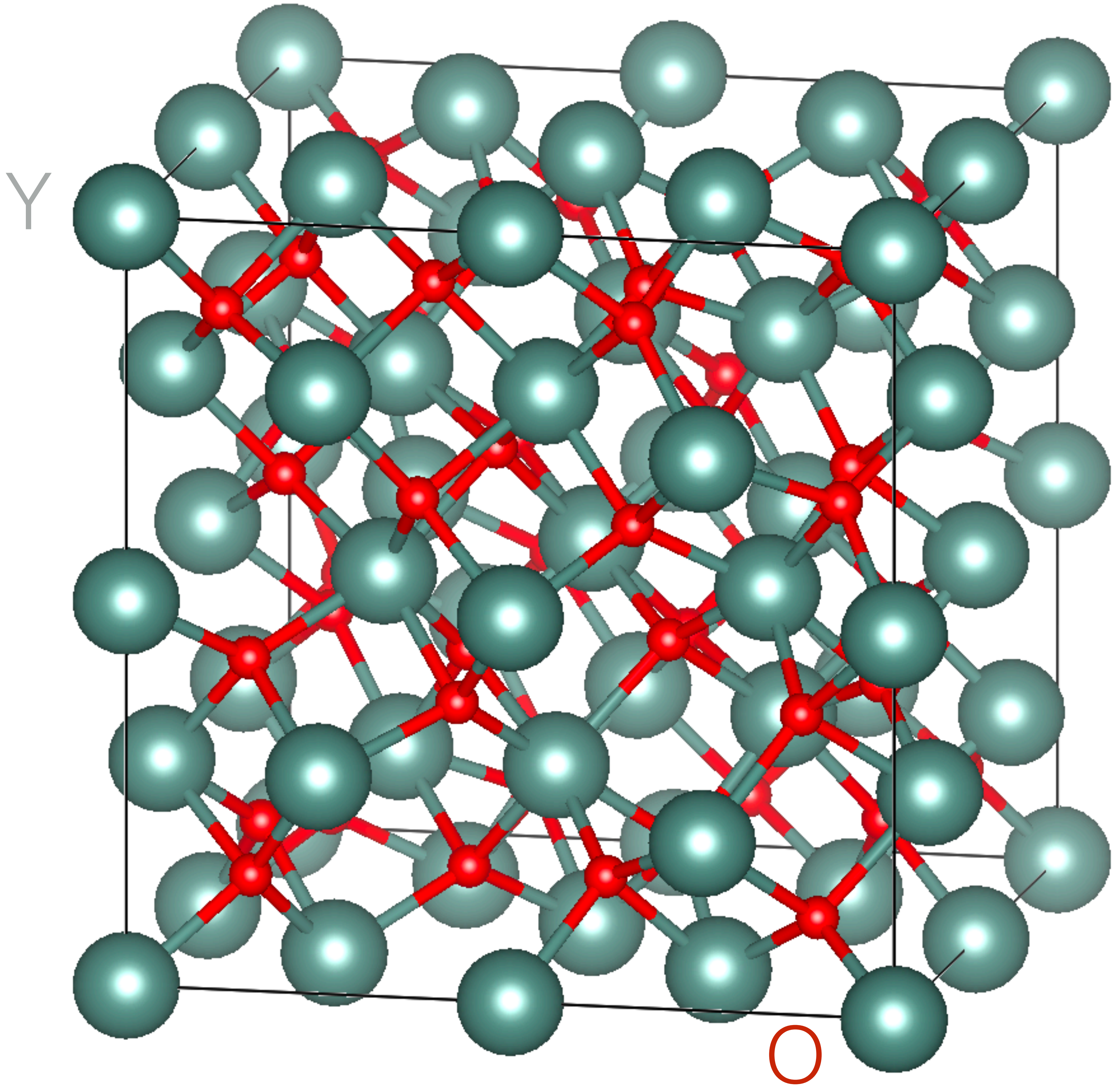




T[K]: 0, 1443, 2633

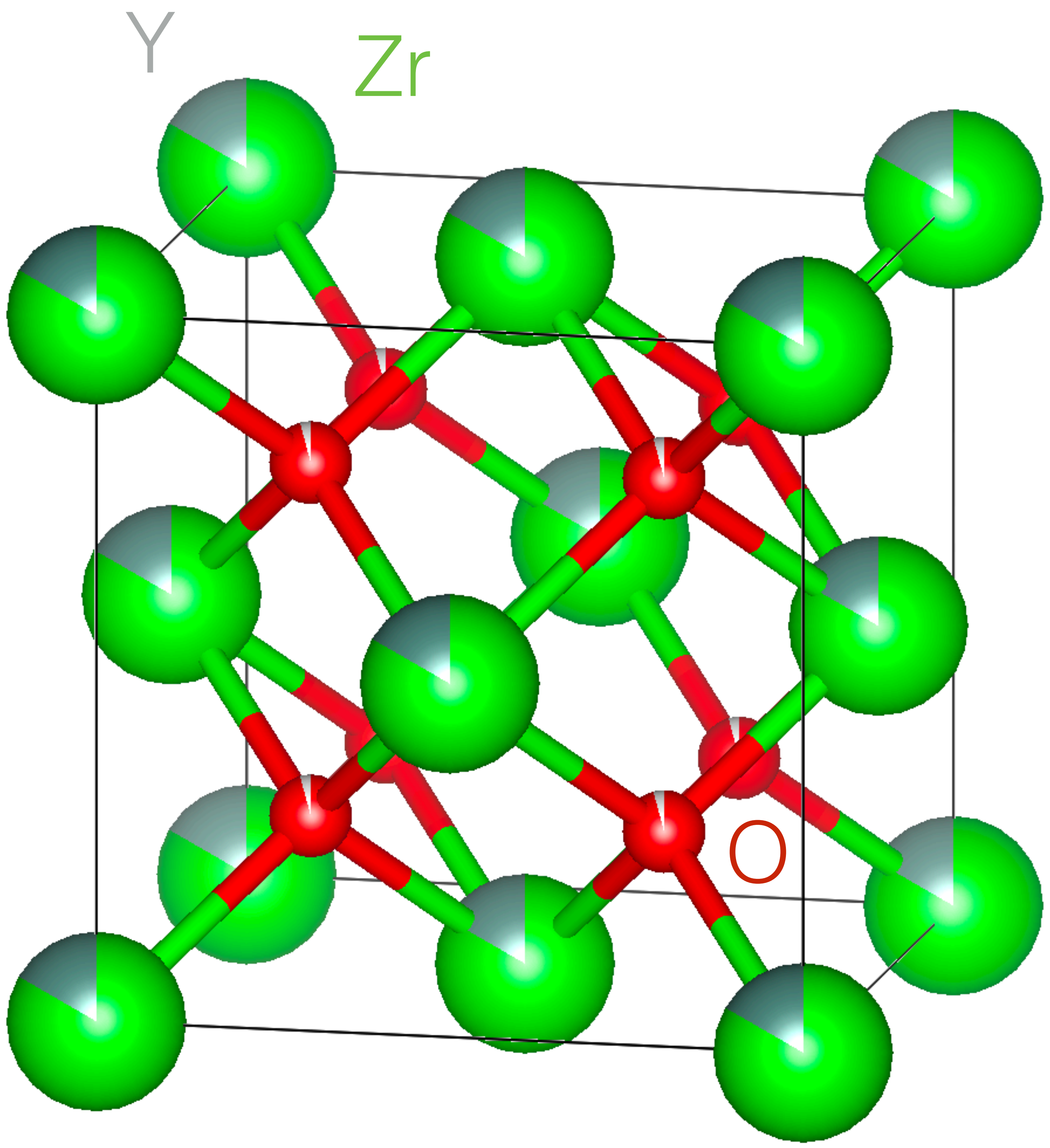
T[°C]: −273, 1170, 2360

Yttrium oxide Y_2O_3 (yttria)



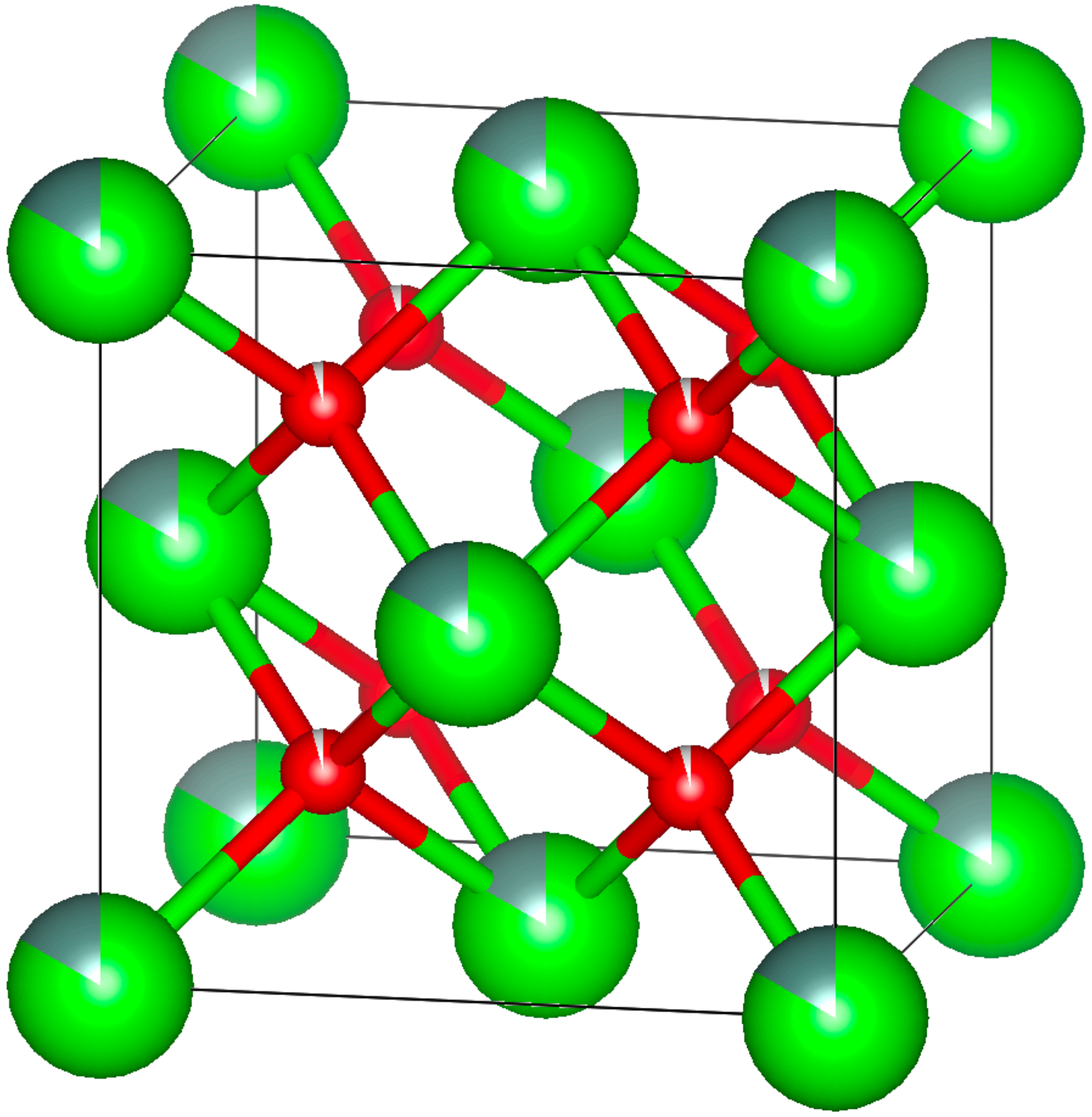
- Cubic structure
- 24 O equivalent sites
- 16 Y sites:
  - 4 are 6-fold coordinated with equal bond lengths
  - 12 are 6-fold coordinated with unequal bond lengths (3 pairs)

Yttria-stabilised zirconia (YSZ)



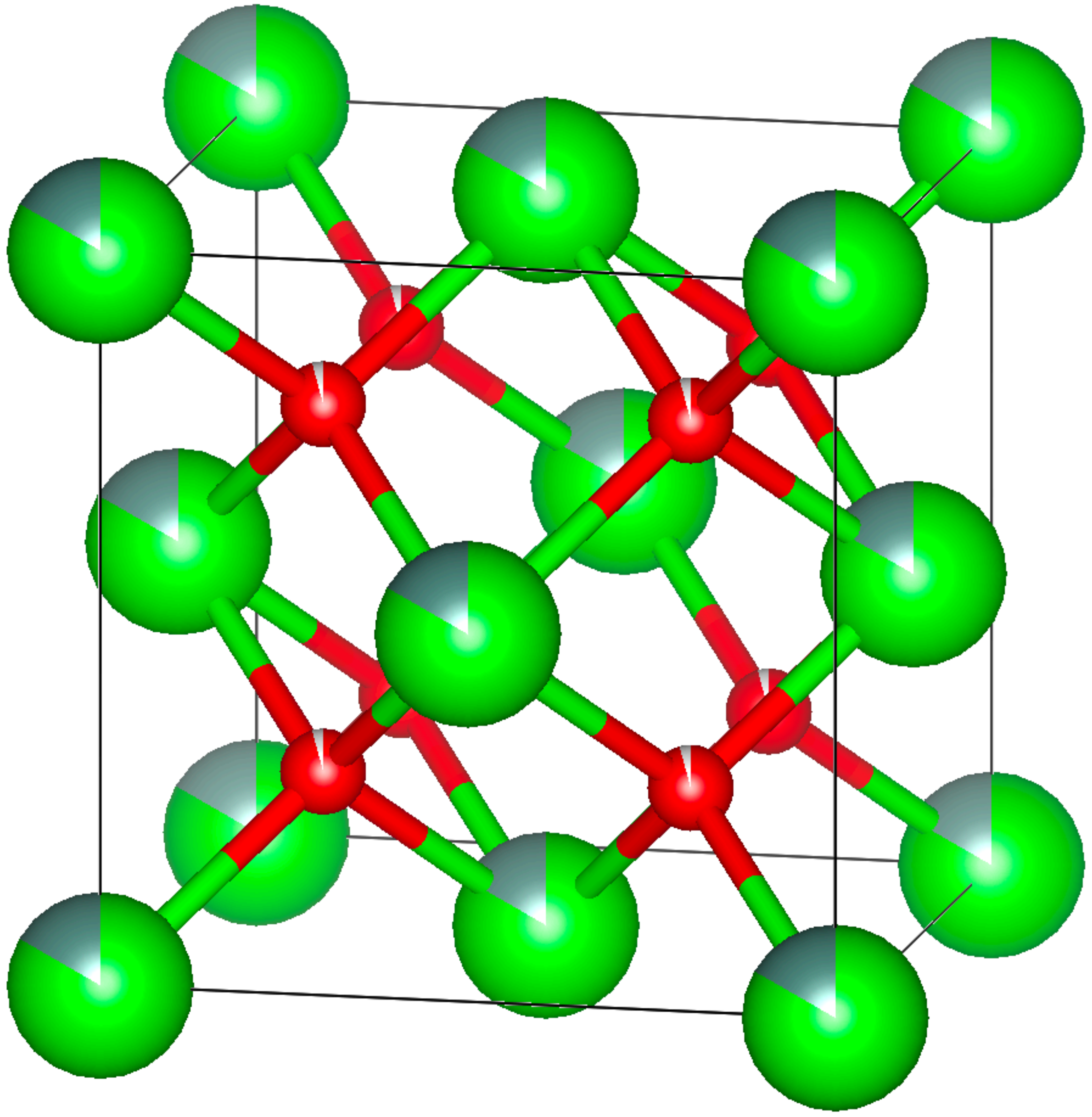
- Add yttria to zirconia
- Cubic fluorite structure
- Room temperature

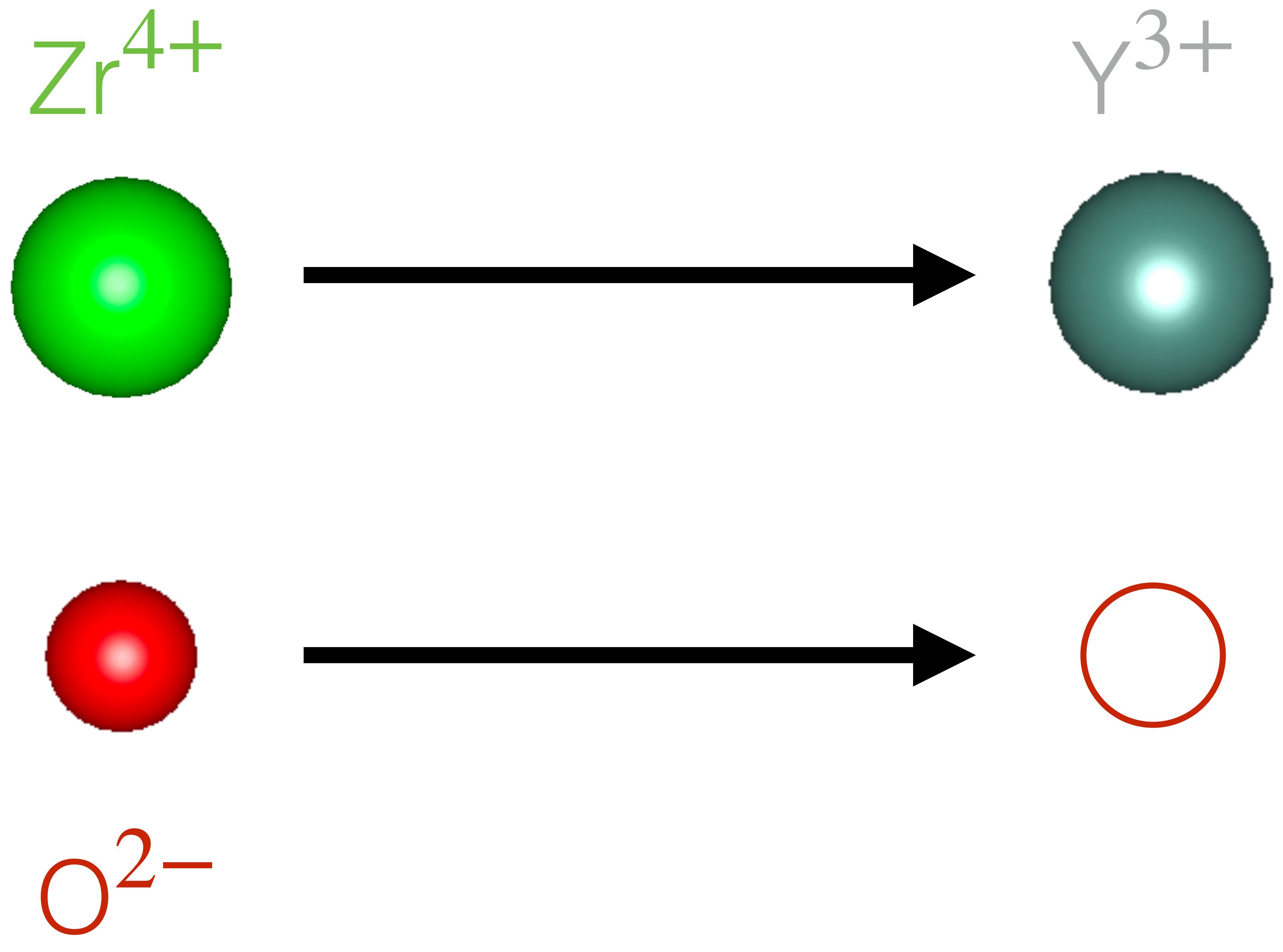
Yttria-stabilised zirconia (YSZ)



- Lost positive charge: $+1$
- Lost negative charge: 0

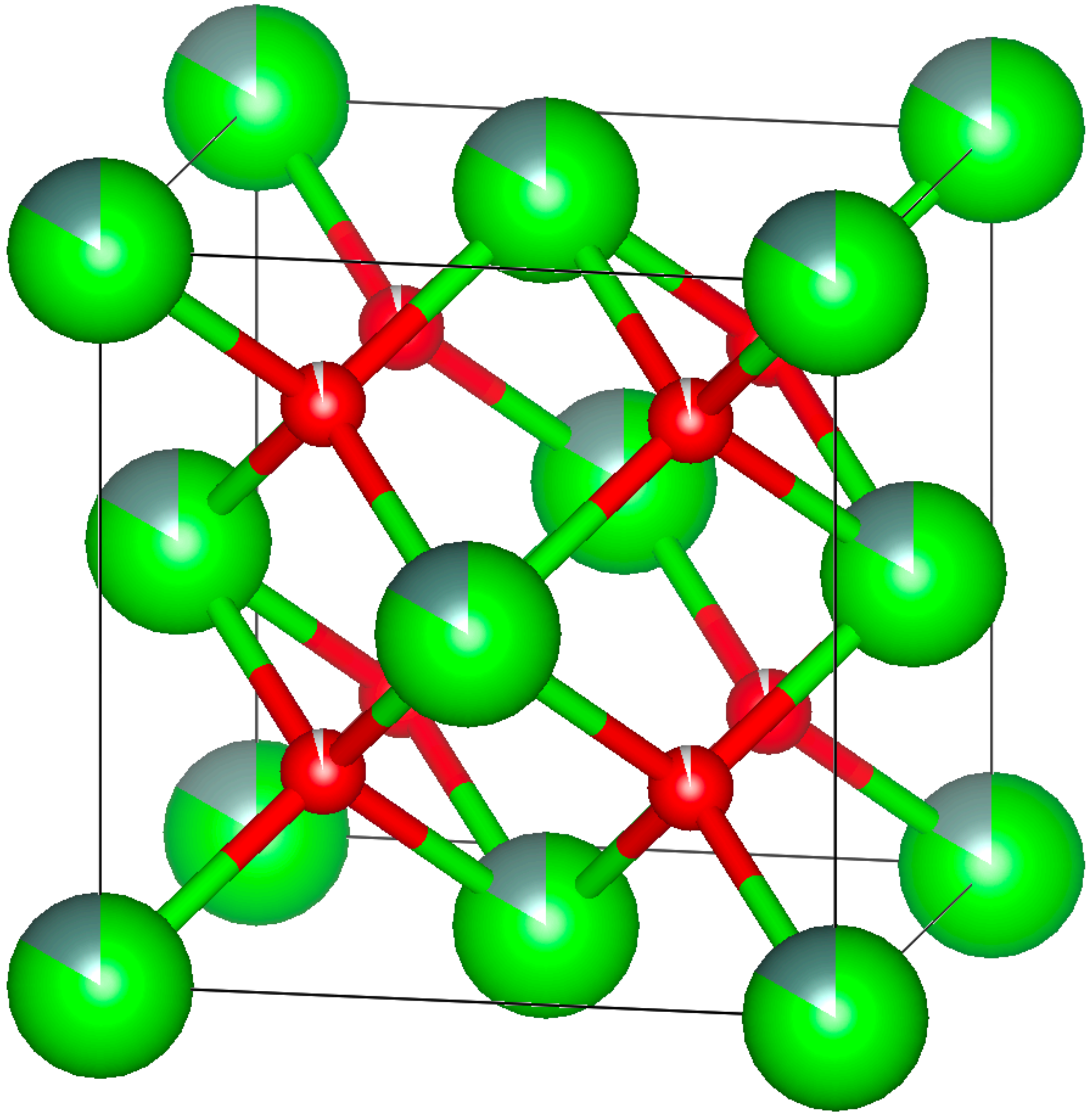
Yttria-stabilised zirconia (YSZ)

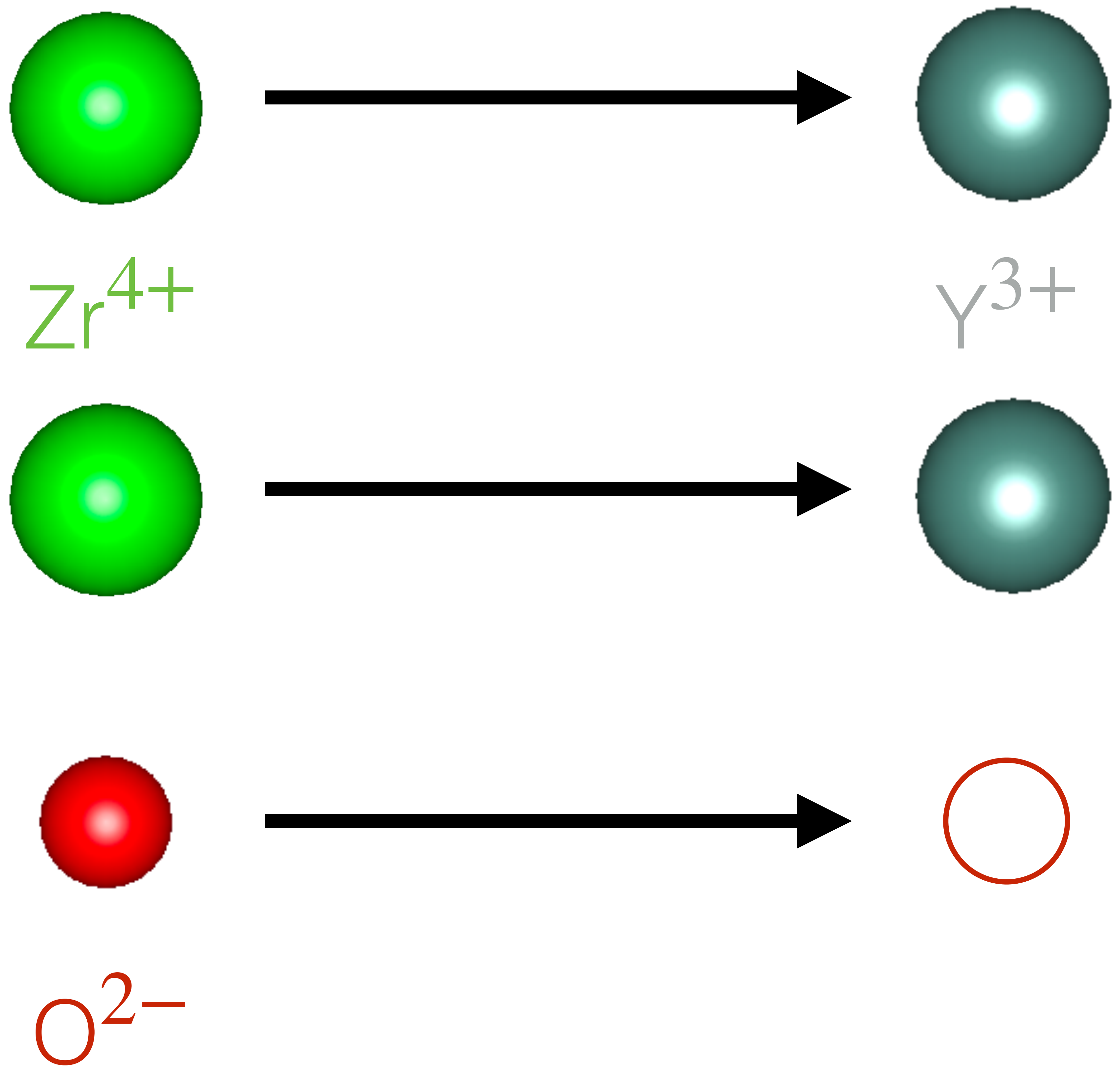




- Lost positive charge: $+1$
- Lost negative charge: -2

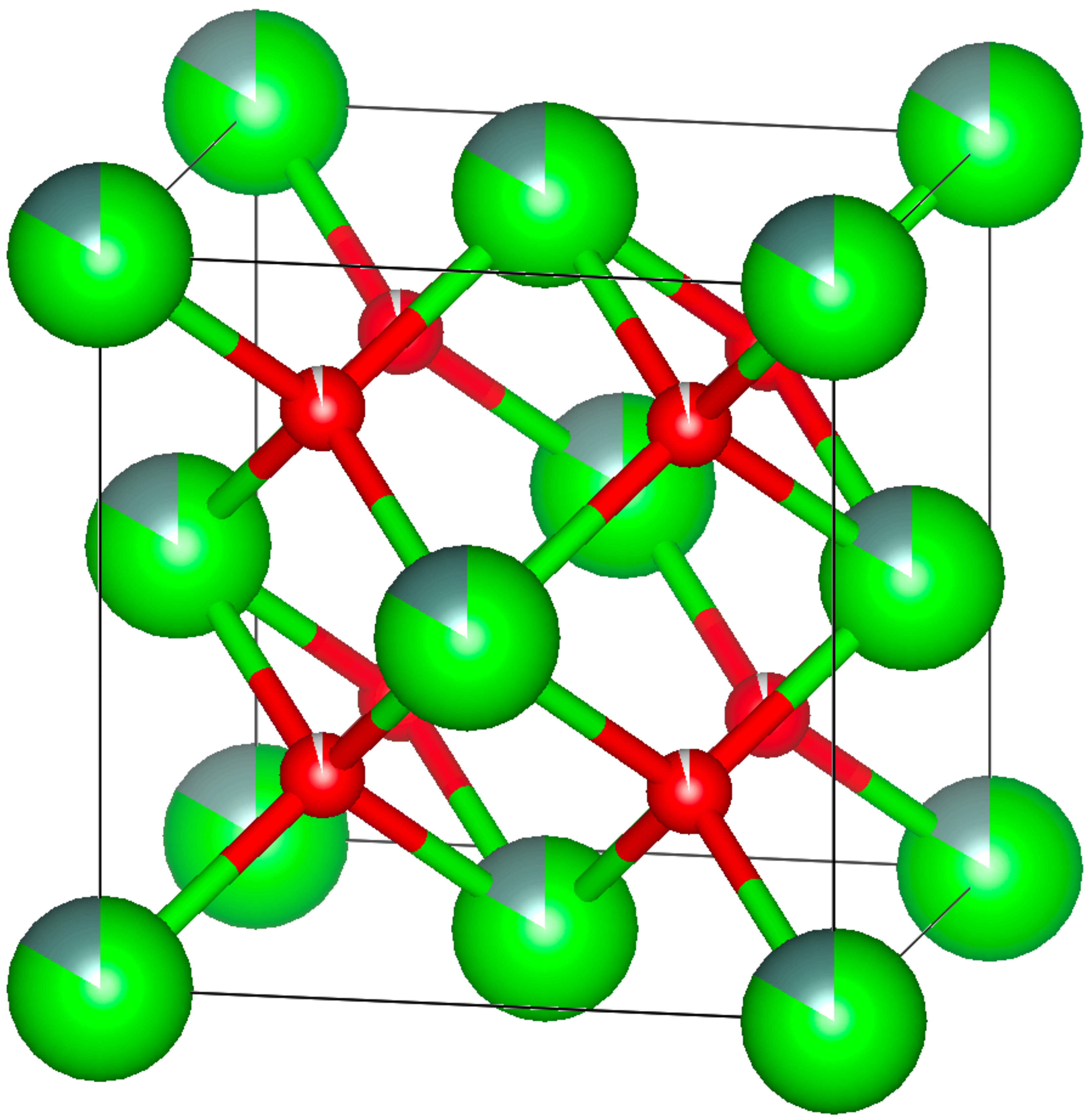
Yttria-stabilised zirconia (YSZ)

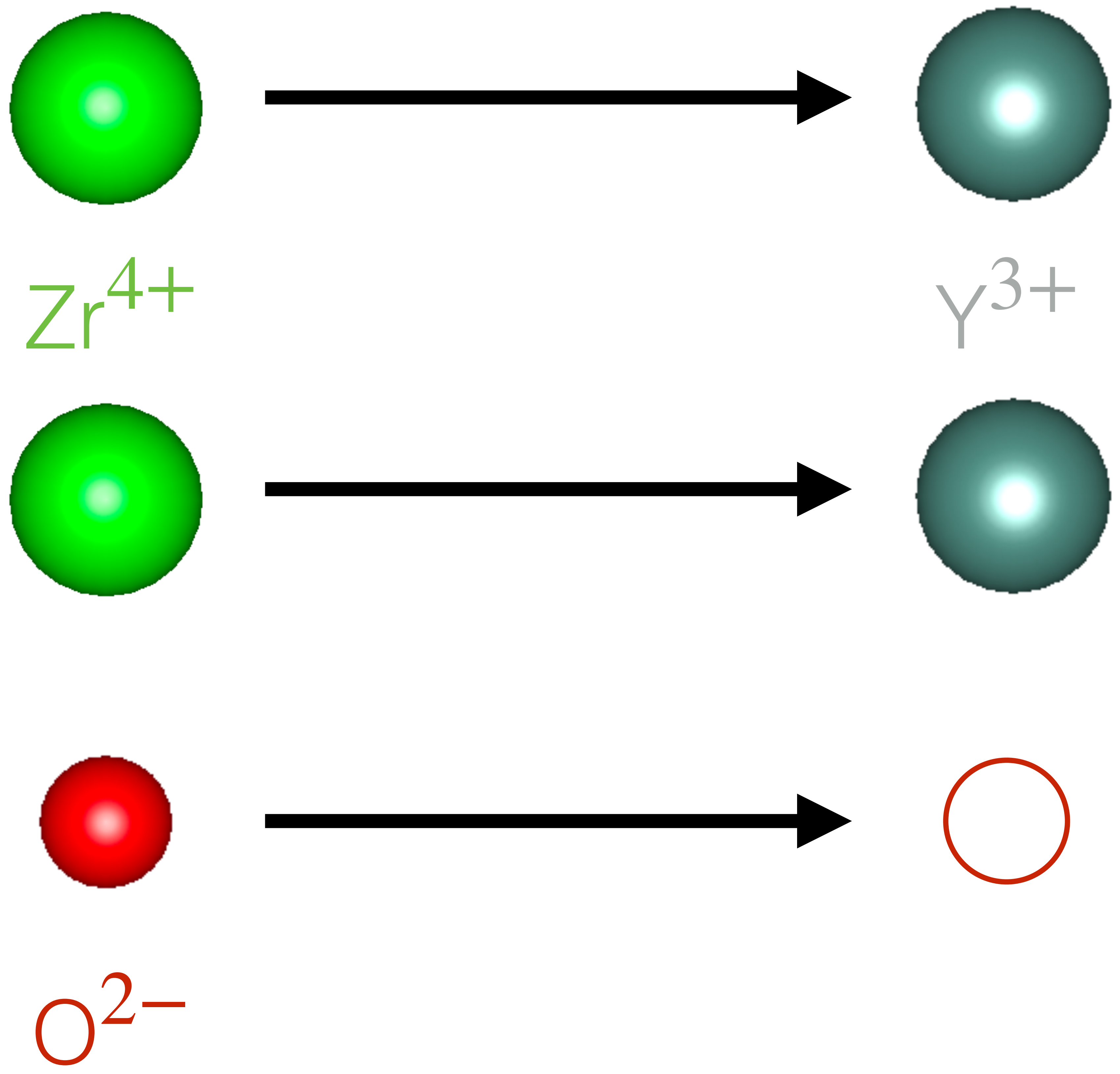




- Lost positive charge: $+2$
- Lost negative charge: -2

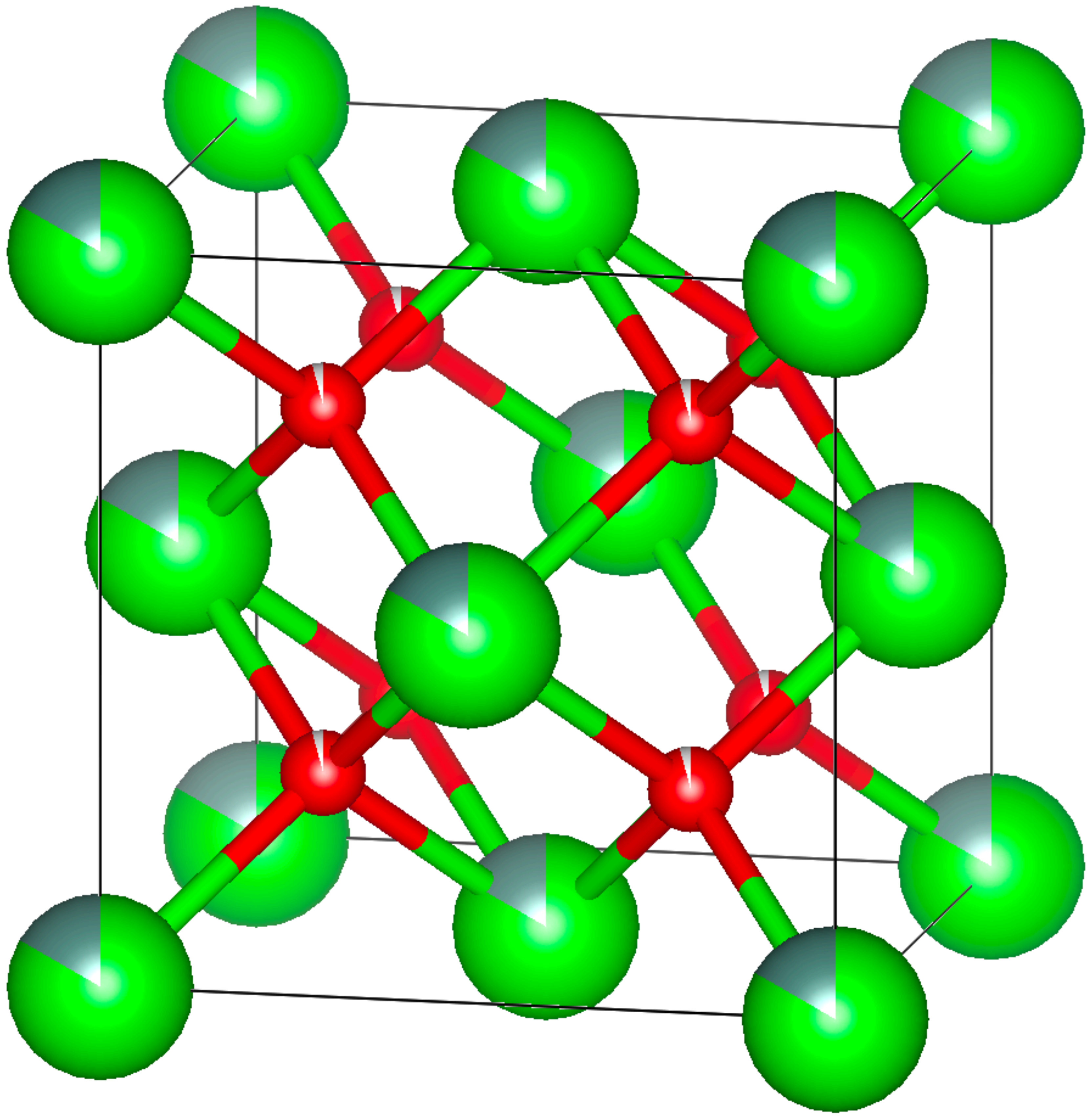
Yttria-stabilised zirconia (YSZ)





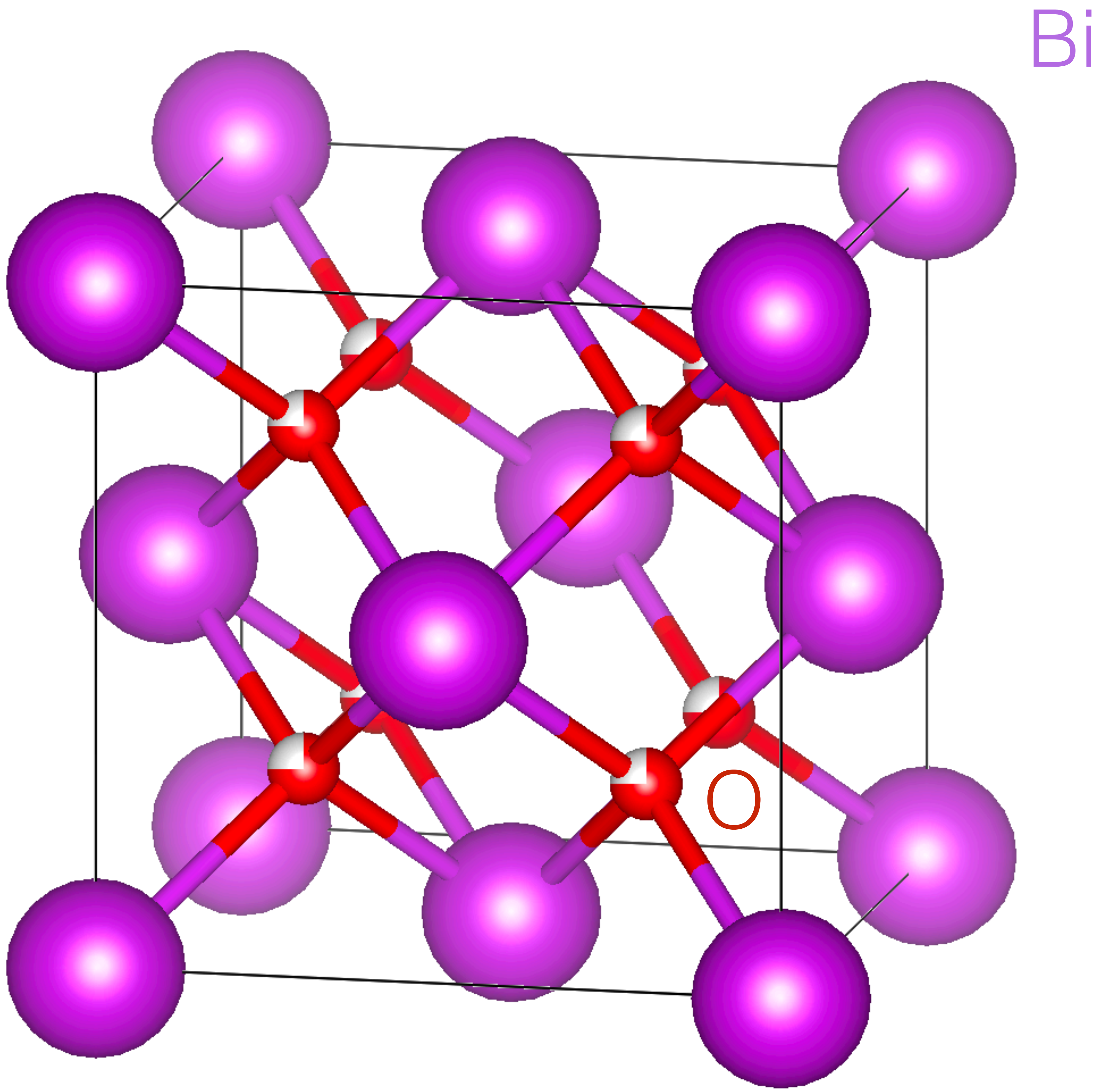
For every 2 Zr^{4+} ions we replace by 2 Y^{3+} ions, we create an oxygen O^{2-} vacancy

Yttria-stabilised zirconia (YSZ)



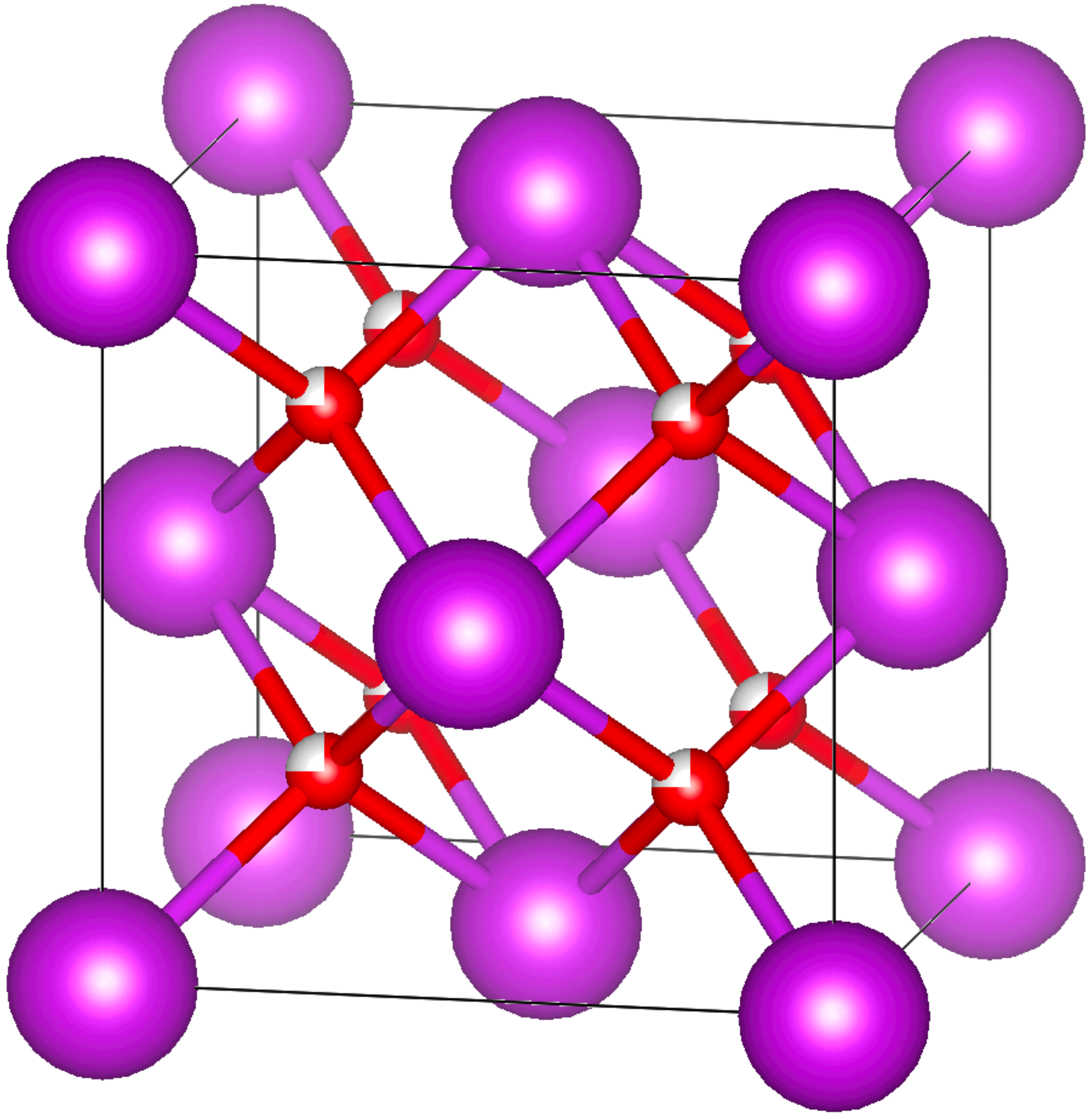
- Yttria-stabilised zirconia
- Oxygen vacancies mediate ionic conduction

δ-Bi_2O_3



- Bi sublattice is fcc
- 8 tetrahedral interstices
- 6 tetrahedral interstices occupied by O
- Fluorite structure (Course A)

δ-Bi_2O_3

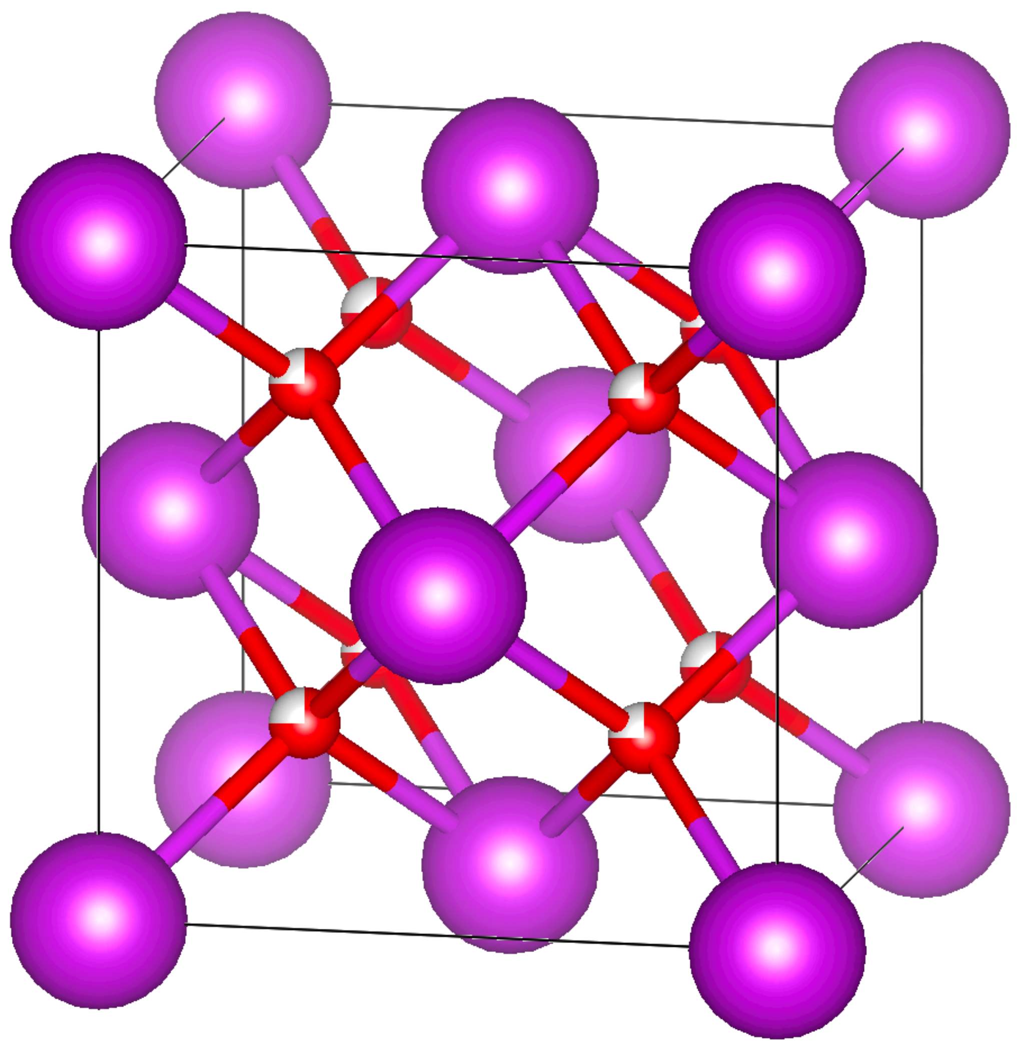


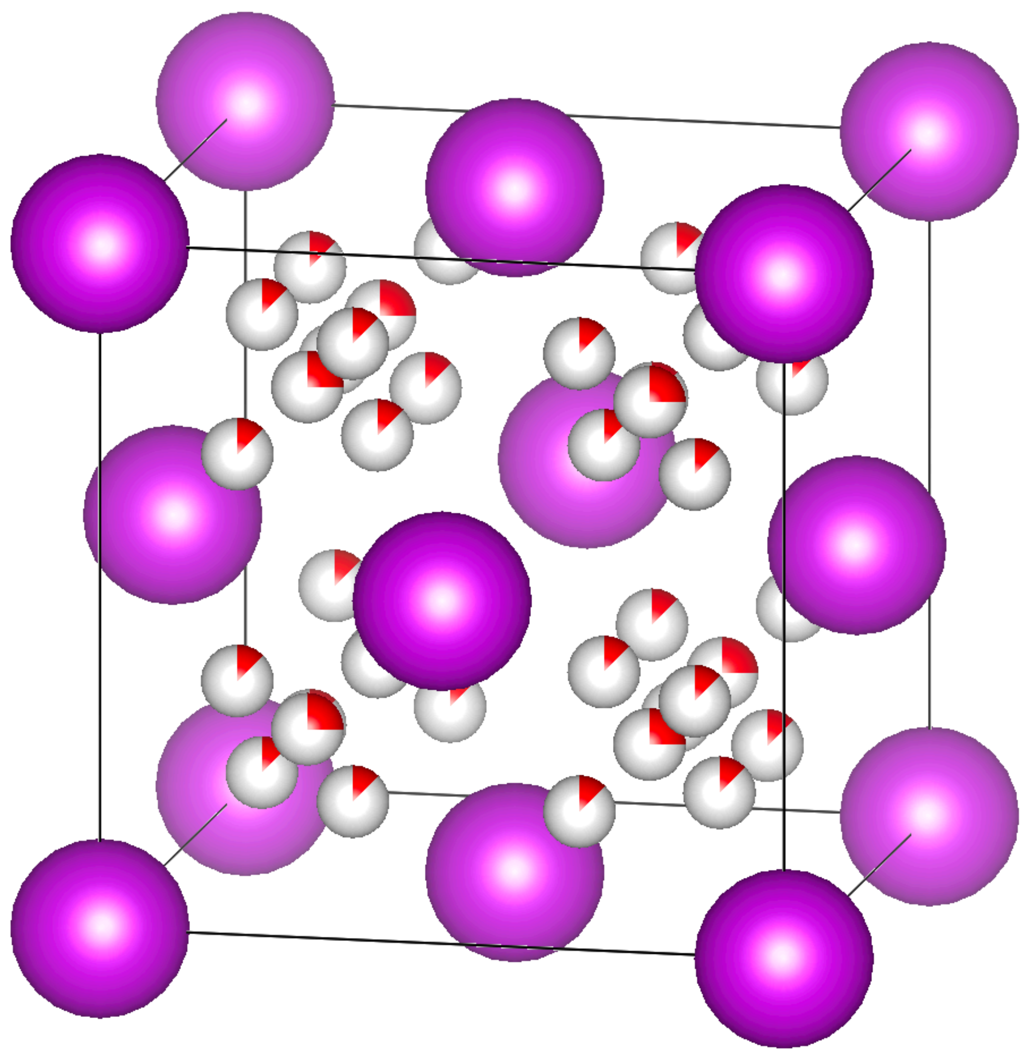
$6\ O^{2-}$ $\quad$ $4\ Bi^{3+}$

- Charge balance:

$$6 \times (-2) + 4 \times (+3) = -12 + 12 = 0$$

δ-Bi_2O_3: competing models

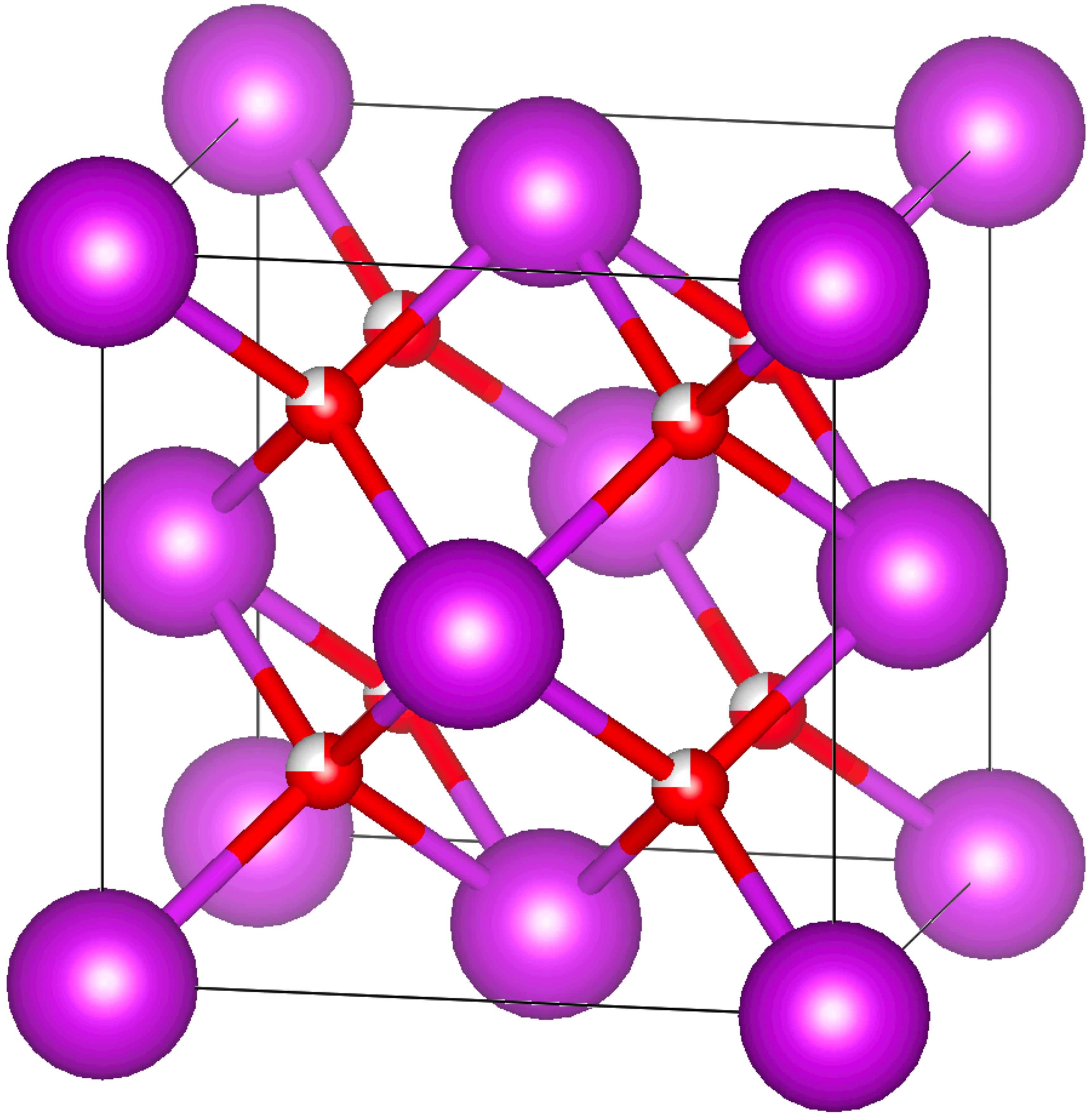




- Ideal tetrahedral sites
- 6/8 tetrahedral interstices occupied

- Sites available that are displaced from ideal tetrahedral sites
- Different distorted sites have different occupation probabilities

δ-Bi_2O_3



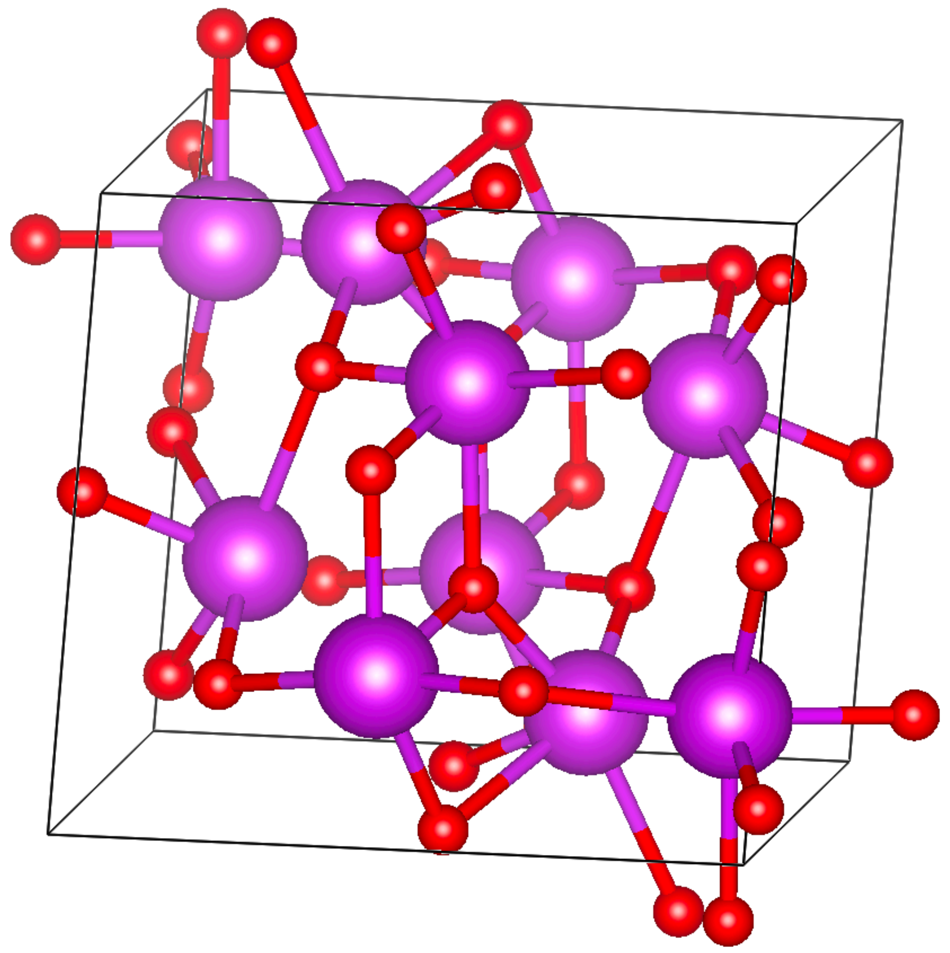
- δ-Bi_2O_3
- Average of 6/8 oxygens per cell
- Oxygen vacancies mediate ionic conduction

Phase diagram of Bi_2O_3: heating

monoclinic (α-Bi_2O_3)

$a \neq b \neq c$

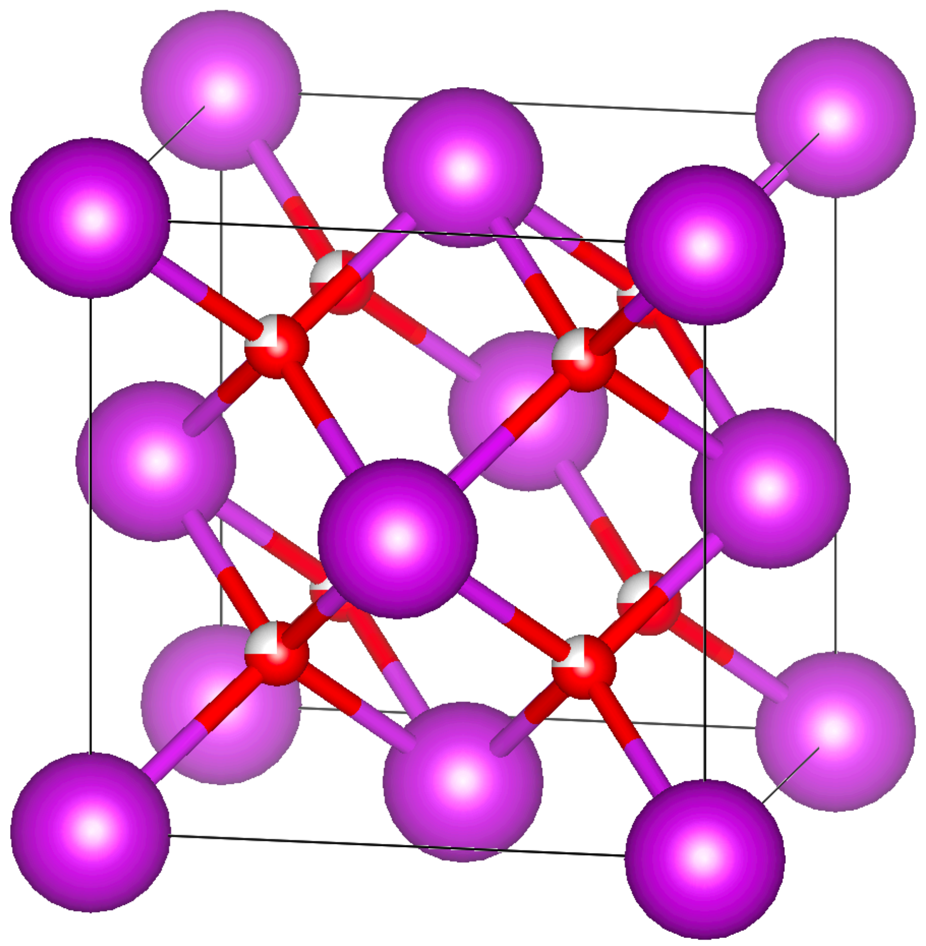
$\alpha = \beta = 90^\circ \neq \gamma$

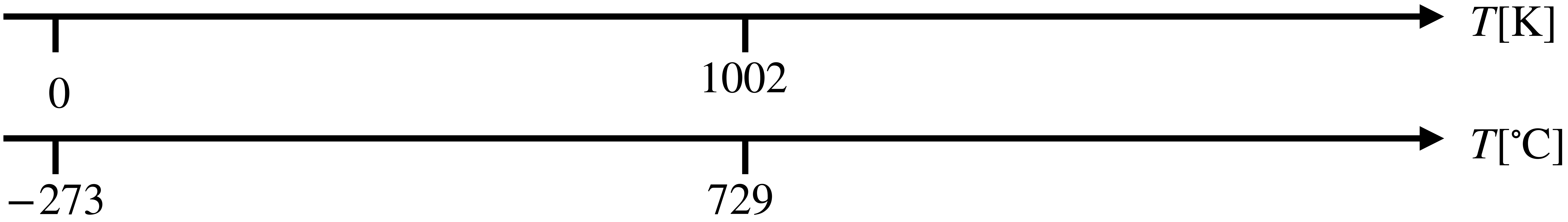


cubic (δ-Bi_2O_3)

$a = b = c$

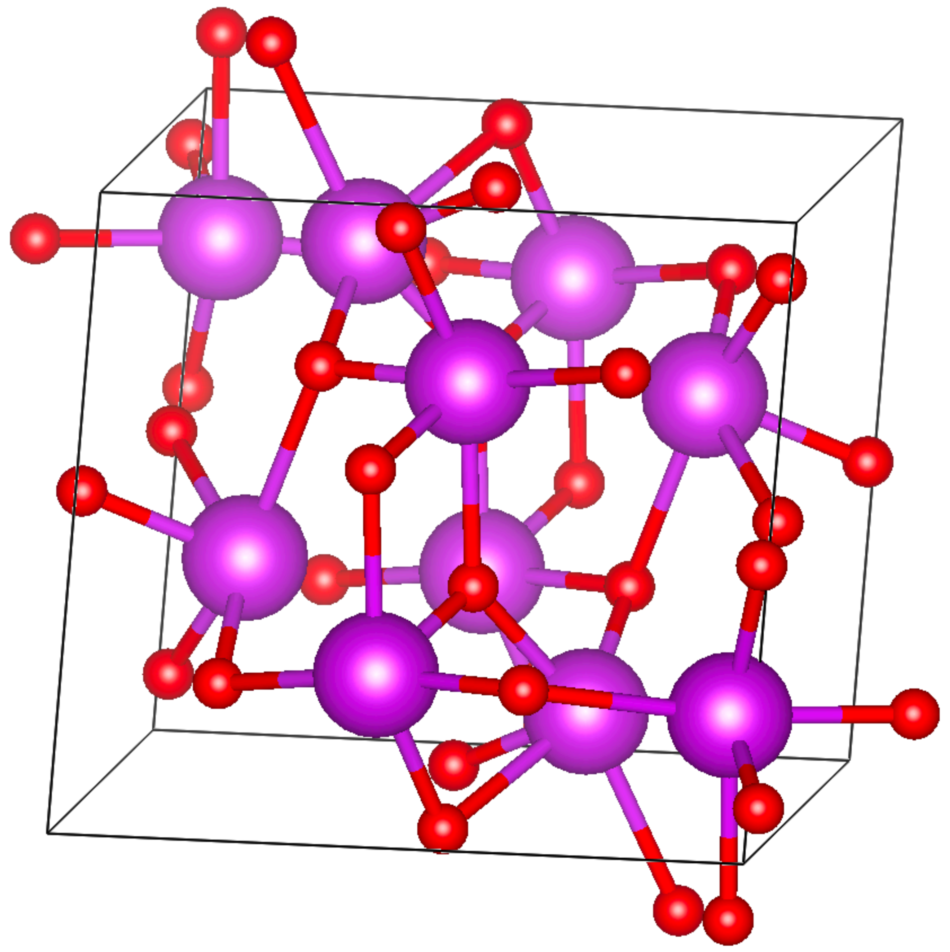
$\alpha = \beta = \gamma = 90^\circ$

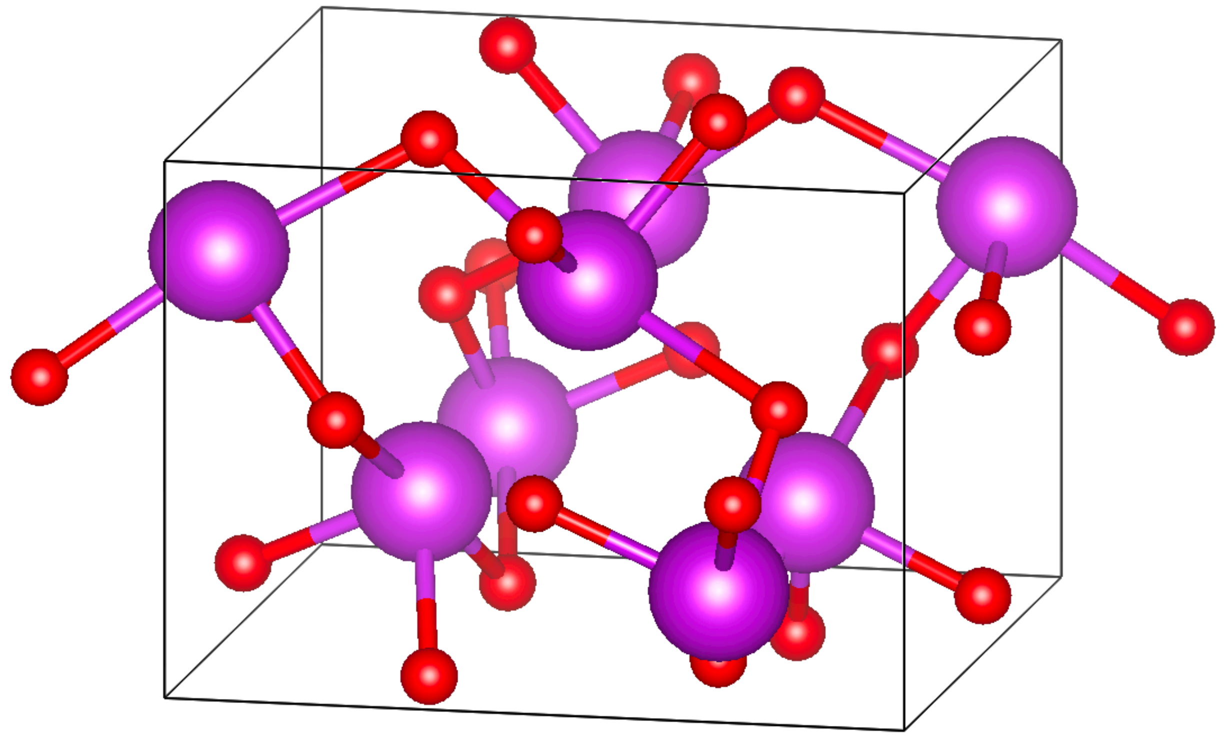


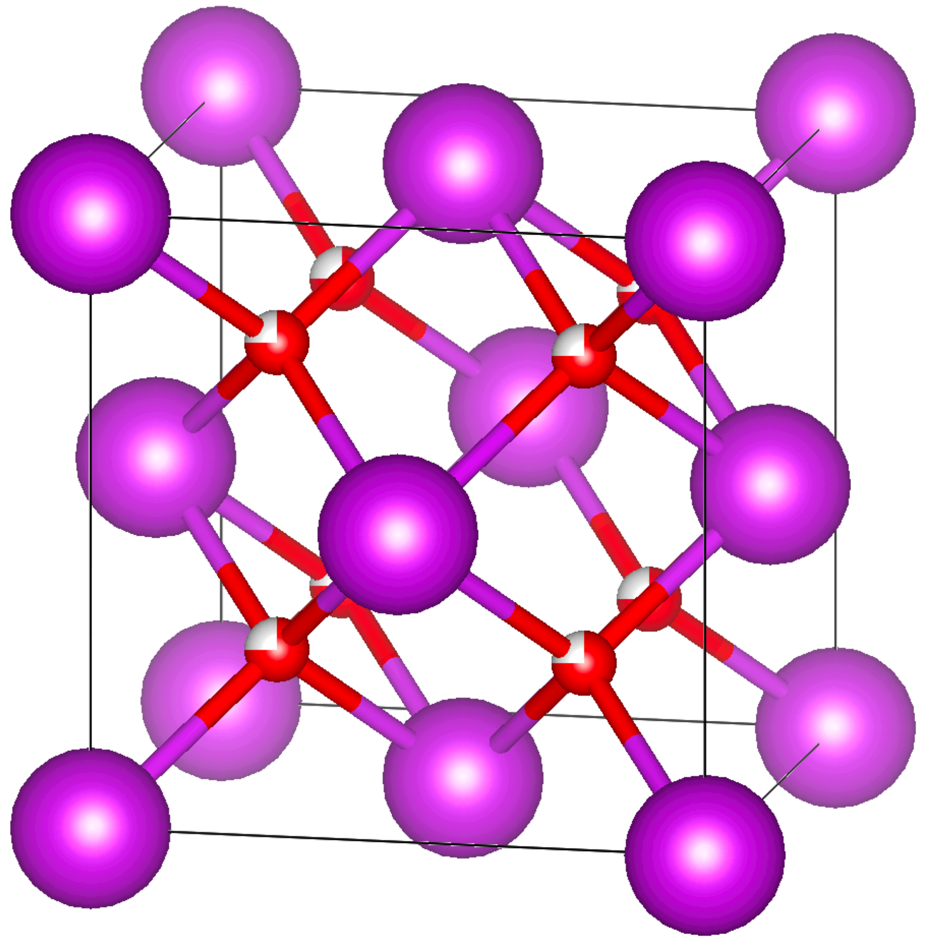


Phase diagram of Bi_2O_3: cooling

monoclinic (α-Bi_2O_3)	tetragonal (β-Bi_2O_3)	cubic (δ-Bi_2O_3)
$a \neq b \neq c$	$a = b \neq c$	$a = b = c$
$\alpha = \beta = 90^\circ \neq \gamma$	$\alpha = \beta = \gamma = 90^\circ$	$\alpha = \beta = \gamma = 90^\circ$







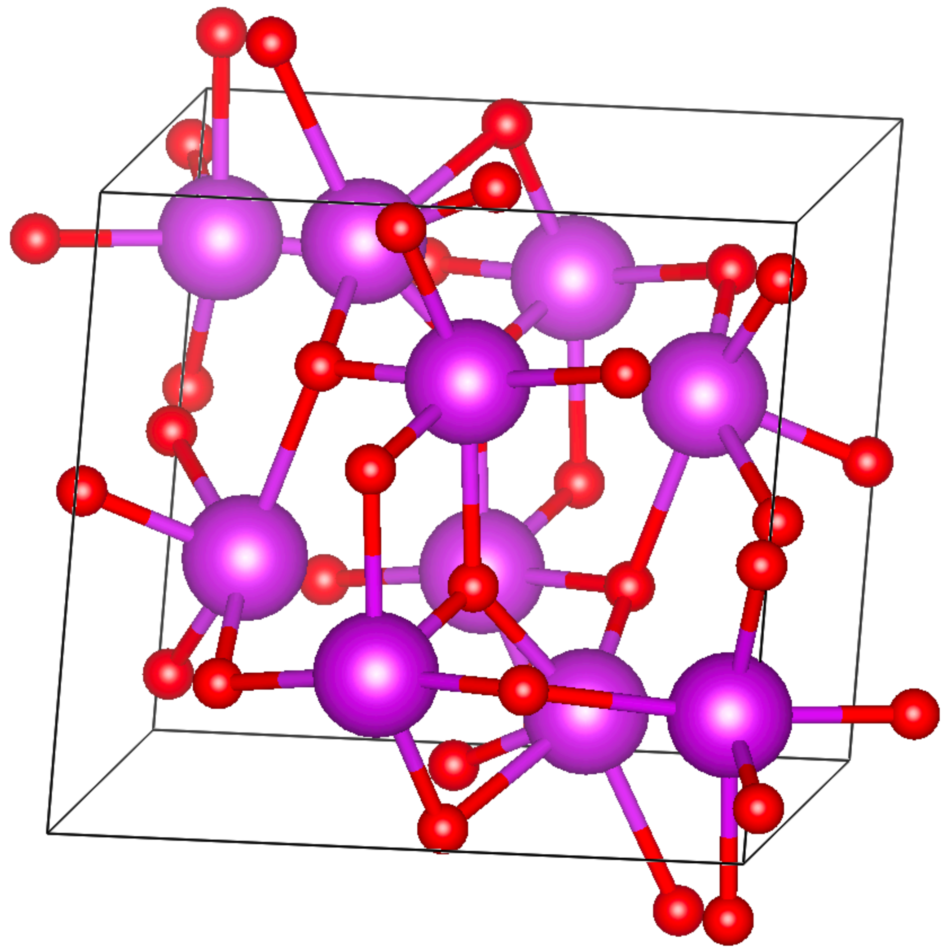
T[K]: 0, 576, 923

T[°C]: -273, 303, 650

Phase diagram of Bi_2O_3: cooling

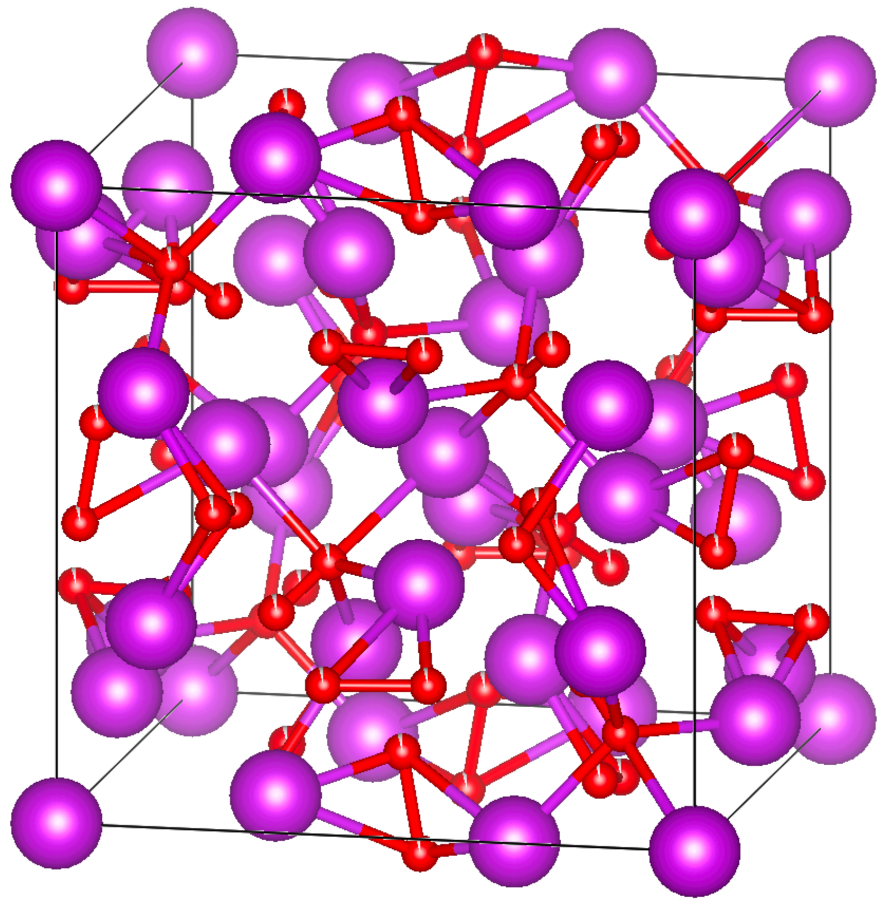
monoclinic (α-Bi_2O_3)

$$a \neq b \neq c$$
$$\alpha = \beta = 90^\circ \neq \gamma$$



cubic (γ-Bi_2O_3)

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$



cubic (δ-Bi_2O_3)

$$a = b = c$$
$$\alpha = \beta = \gamma = 90^\circ$$