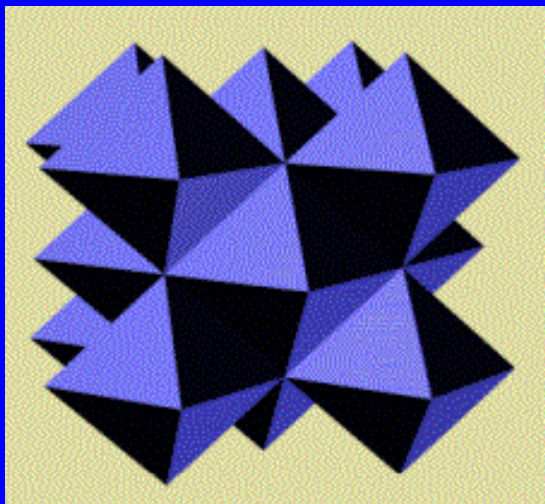
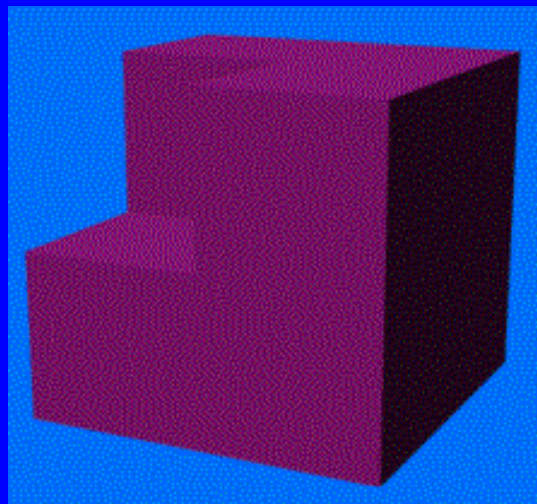


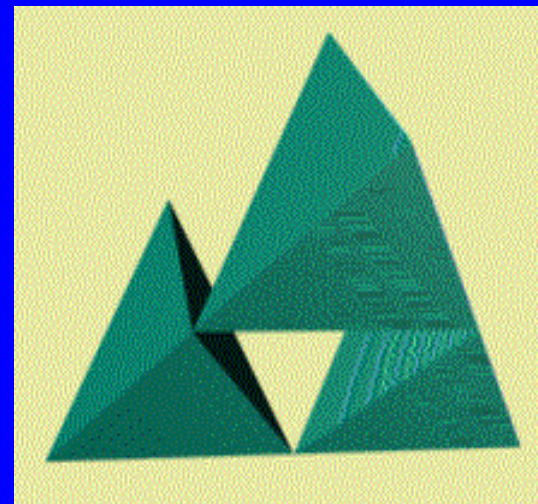
# 鲍林规则及缺陷反应（补充）



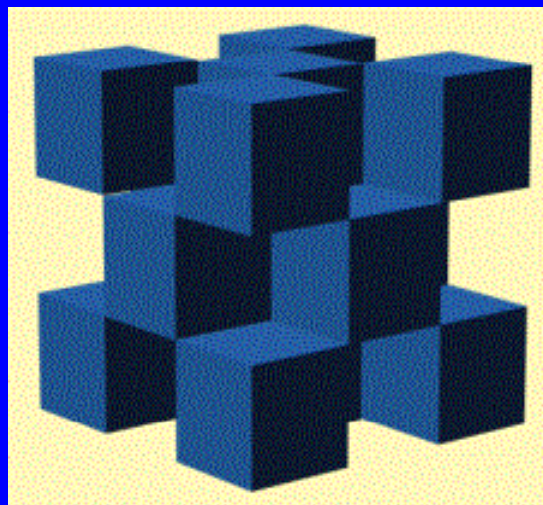
NaCl



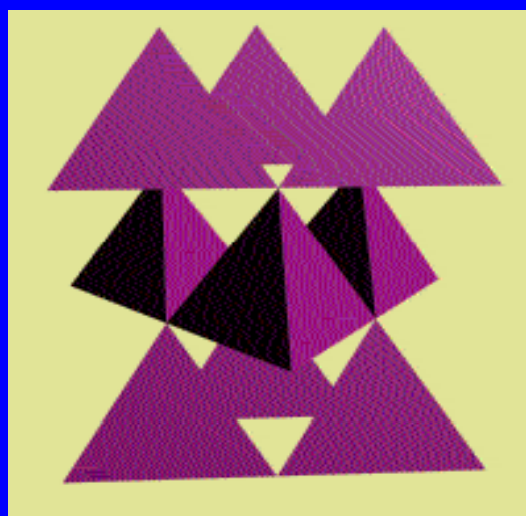
CsCl



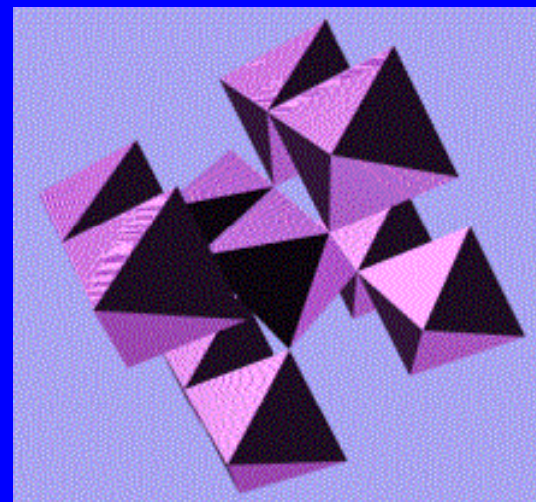
闪锌矿



CaF<sub>2</sub>



纤锌矿



金红石

# Electrostatic Bond Valence Principle

**Pauling 第二规则（电价规则）**：设 $Z_+$ 为正离子

带的电荷数， $u$ 为其配位数，从正离子到每一个

配位负离子间的静电键强度 $S$ 定义为：

Bond valence; bond strength

$$S = \frac{Z_+}{u}$$

或者，在一个稳定的离子型结构中，负离子的

电价等于或近乎等于从邻近的正离子至该负离子各

静电键强度之总和：即

$$Z_- = \sum_i S_i = \sum_i \frac{Z_{+i}}{u_i}$$

实际上，该规则对正离子的电价也成立：

$$Z_+ = \sum_i S_i = \sum_i \frac{Z_{-i}}{u_i}$$

$Z_-$ 为负离子电荷数（电价）， $S_i$ 指某一负离子至每一个以负离子为顶点的多面体中央的正离子的静电键强度(**electrostatic bond strength, *ebs***)，这就是**电价规则**。

**Example 1:** NaCl, 其静电键强度为

$$S_i = \frac{1}{6}$$

则 $\text{Cl}^-$ 的电价

$$Z_{\text{Cl}^-} = \sum_i S_i = 6 \times \frac{1}{6} = 1$$

上下、前后、左右共6个八面体共用一个 $\text{Cl}^-$ 顶点。

## Bond Valence – Example 2

Consider the rutile form of  $\text{TiO}_2$ . What is the valence of the Ti-O bonds?

First let's calculate the valence of the Ti-O bonds.

$$V_i = \sum s_{ij}$$

$$4 = 6(s_{ij})$$

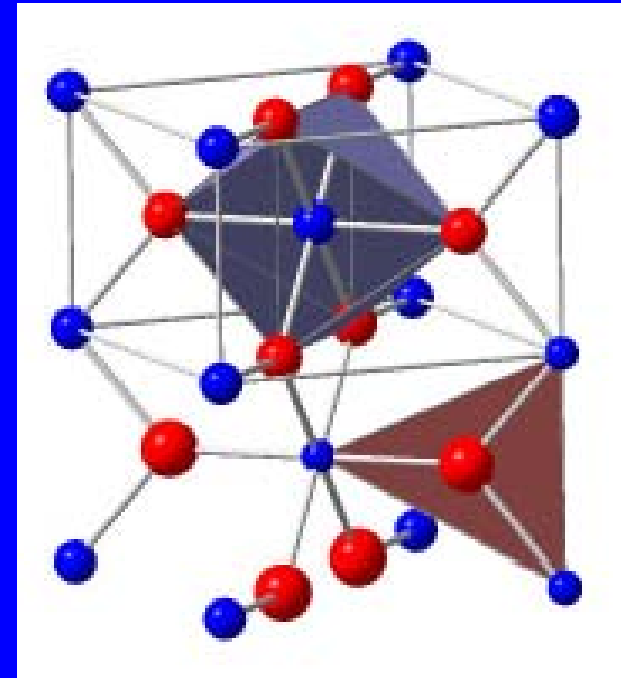
$$s_{ij} = 2/3$$

Now use this to determine the coordination number of oxygen.

$$V_i = \sum s_{ij}$$

$$2 = n (2/3)$$

$$n = 3$$



Other rutile  $\text{MX}_2$ :  $\text{SnO}_2$ ,  $\text{PbO}_2$ ,  $\text{RuO}_2$ ,  $\text{MgF}_2$ ,  $\text{NiF}_2$ , etc.

## Bond Valence – Example 3

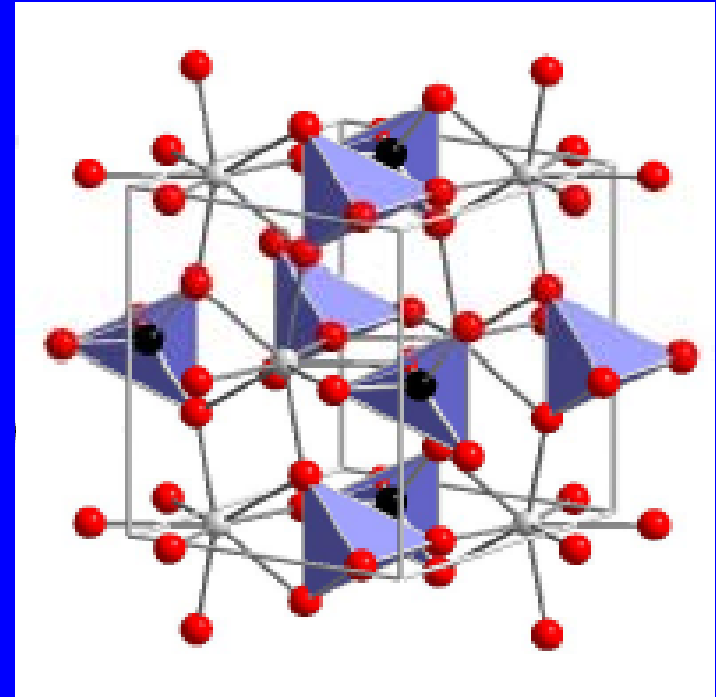
What is the oxygen coordination in the mineral zircon (锆石, 锆英石),  $ZrSiO_4$ , where  $Si^{+4}$  is tetrahedrally coordinated and  $Zr^{+4}$  is eight coordinated?

First lets calculate the valence of the Si-O bonds.

$$V_i = \sum s_{ij}$$

$$4 = 4(s_{Si-O})$$

$$s_{Si-O} = 1$$





Now lets calculate the valence of the Zr-O bonds.

$$V_i = \sum s_{ij}$$

$$4 = 8 (s_{Zr-O})$$

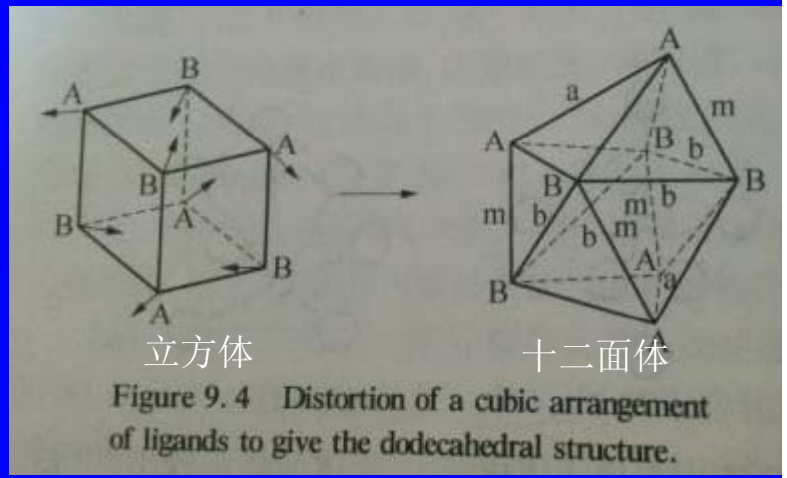
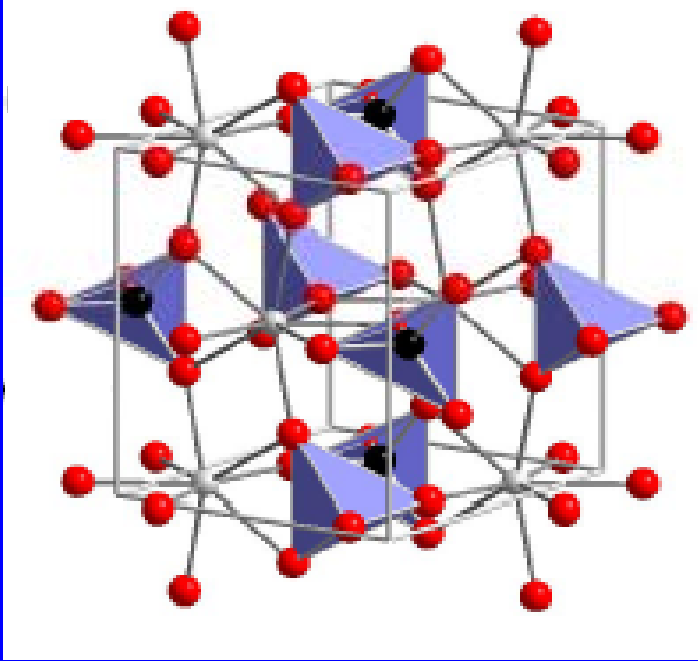
$$s_{Zr-O} = 1/2$$

Now lets calculate the coordination number of oxygen.

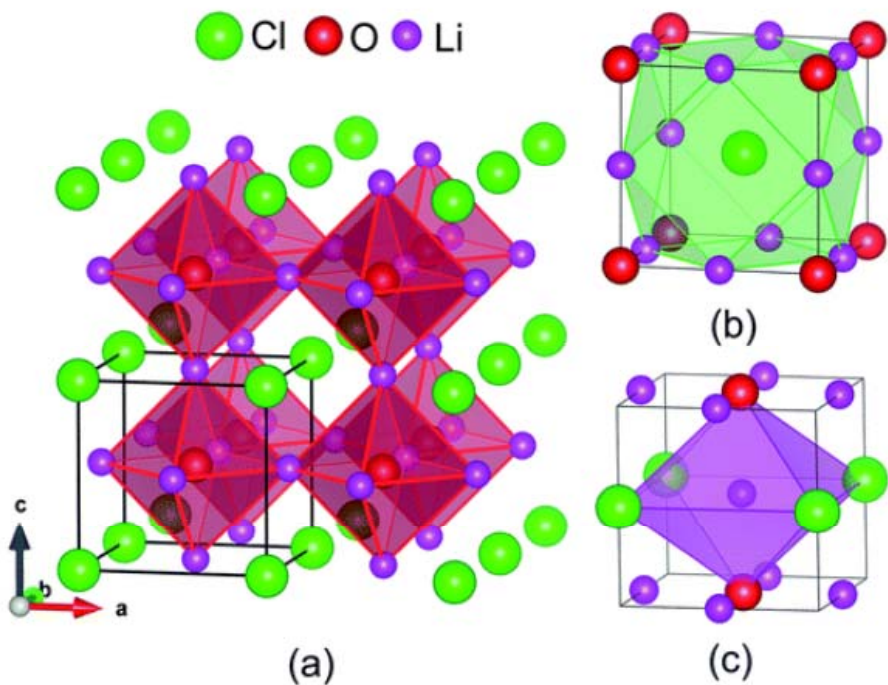
$$V_i = n_1 s_{Si-O} + n_2 s_{Zr-O}$$

$$2 = n_1 (1) + n_2 (1/2)$$

$$n_1=1 \quad n_2=2$$



# A new Li-ionic conductor: $\text{Li}_3\text{OCl}$



**Fig. 1** (a) The crystal structures of  $\text{Li}_3\text{OCl}$  with  $\text{Li}_6\text{O}$  octahedron, (b)  $\text{Li}_{12}\text{Cl}$  cuboctahedron, and (c)  $\text{LiO}_2\text{Cl}_4$  octahedron coordination environments. The cube enclosed by solid black lines denotes a unit cell. The small purple balls denote Li ions, while the medium sized red and big sized green balls are O ions and Cl ions, respectively. All Li, O, and Cl atoms are represented with the spheres of the same color and size in the following of this paper.

求锂离子周围的阴离子配位?

$$V_{\text{Li}} = n_1 s_{\text{Li-O}} + n_2 s_{\text{Li-Cl}}$$

$$1 = n_1 (1/3) + n_2 (1/12)$$

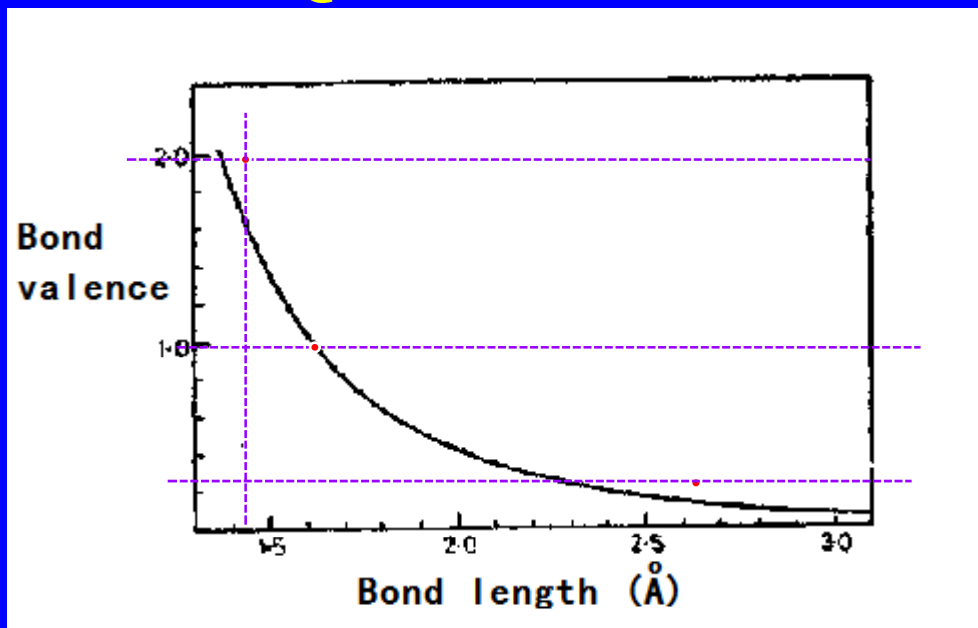
$$12 = 4 n_1 + n_2$$

Hence,  $n_1=2$   $n_2=4$

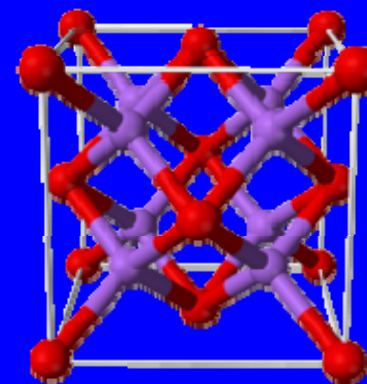
An antiperovskite structure:  $\text{Li}_6\text{O}$ ,  $\text{Li}_{12}\text{Cl}$ ,  $\text{LiO}_2\text{Cl}_4$

# § Pauling第二规则的发展和应用

## — 定量键价方法 (Quantitative Bond Valence Method)



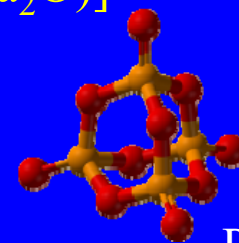
West, p.231



Na<sub>2</sub>O (反萤石结构)

氧与第二周期原子Na, Mg, Al, Si, P, S之间的键价-键长关系 (I.D. Brown, 1978) [O-M键长: 1.43(SO<sub>2</sub>); 1.60, 1.62(SiO<sub>2</sub>); 2.65(Na<sub>2</sub>O)]

$$s_{ij} = (R_0 / R)^N$$



P<sub>2</sub>O<sub>5</sub>

- 式中R是键长，R<sub>0</sub>、N为常数 (R<sub>0</sub>是单位键价的键长值)；
- 对上图代表的元素，R<sub>0</sub>=1.622, N=4.290。



A powerful advance on Pauling's bond valence method is to quantitatively link the bond valence to the bond distance (rather than the oxidation state). While a number of scientists have helped in this endeavor the principle driving force has largely been I.D. Brown from McMaster University.<sup>1,2</sup> The bond valence is calculated using the following relationship:

$$s_{ij} = \exp [(R_{ij} - d_{ij})/b] \quad (R_{ij}, d_{ij} \text{ in } \text{Å})$$

Where  $d_{ij}$  is the distance between atoms  $i$  and  $j$ ,  $R_{ij}$  is the empirically determined distance for a given cation-anion pair, and  $b$  is also an empirical value generally set equal to **0.37**. Values of  $R_{ij}$  that give bond valence sums near the oxidation state have been tabulated.<sup>3,4,5</sup>

1. I.D. Brown, *Chem. Soc. Reviews* **7**, 359-376 (1978).
2. I.D. Brown, "The chemical bond in inorganic chemistry: the bond valence model" Oxford Univ. Press, New York (2002).
3. Brown & Altermatt, *Acta Cryst. B* **41**, 244-247 (1985).
4. Brese & O'Keefe, *Acta Cryst. B* **47**, 192-197 (1991).
5. O'Keefe, *Acta Cryst. A* **46**, 138-142 (1990).

# Example of Bond Valence Parameters

Li 1	O -2	1.466	0.37	a ?	Mg 2	O -2	1.693	0.37	a ?
Li 1	O -2	1.062	0.642	bs ?	Mg 2	O -2	1.608	0.443	bs ?
Li 1	O -2	1.29	0.48	o ?	Mg 2	O -2	1.636	0.42	o ?
Li 1	S -2	1.94	0.37	b ?	Mg 2	S -2	2.18	0.37	b ?
Li 1	S -2	1.4607	0.656	c '6 A cut-off'	Mg 2	Se -2	2.32	0.37	b ?
Li 1	Se -2	2.09	0.37	b ?	Mg 2	Te -2	2.53	0.37	b ?
Li 1	Se -2	1.6272	0.681	c '7 A cut-off'	Mg 2	F -1	1.578	0.37	a ?
Li 1	Te -2	2.30	0.37	b ?	Mg 2	Cl -1	2.08	0.37	b ?
Li 1	Te -2	1.7340	0.717	c '7 A cut-off'	Mg 2	Br -1	2.28	0.37	b ?
Li 1	F -1	1.360	0.37	a ?	Mg 2	I -1	2.46	0.37	b ?
Li 1	F -1	1.0968	0.503	c '6 A cut-off'	Mg 2	N -3	1.85	0.37	b ?
Li 1	Cl -1	1.91	0.37	b ?	Mg 2	P -3	2.29	0.37	b ?
Li 1	Cl -1	1.94	0.37	e unchecked	Mg 2	As -3	2.38	0.37	b ?
Li 1	Br -1	2.02	0.37	b ?	Mg 2	H -1	1.53	0.37	b ?
Li 1	Br -1	1.5150	0.674	c '7 A cut-off'					
Li 1	I -1	2.22	0.37	b ?	H 1	O -2	0.957	0.35	az 'From gas and
Li 1	I -1	1.6754	0.722	c '7 A cut-off'					symmetrical bond
Li 1	N -3	1.61	0.37	b ?					
Li 1	N -3	1.15	0.631	ay '6.5 A cut-off'					

## 推导

$$\begin{aligned}\ln S_{ij} &= N \ln \frac{R_0}{R} = -N \ln \frac{R}{R_0} = -N \ln \left( 1 + \frac{R-R_0}{R_0} \right) \\ &= -N \left( \frac{R-R_0}{R_0} \right) = - \left( \frac{R-R_0}{R_0/N} \right)\end{aligned}$$

$$\begin{aligned}b &\approx R_0/N \\ &= 1.622/4.29 \\ &= 0.378\end{aligned}$$

Therefore  $s_{ij} = \exp [(R_{ij} - d_{ij})/b]$

# Uses of the Bond Valence Method

1. To examine experimental structures for accuracy, determine oxidation states, or identify bonding instabilities.
2. To locate light atoms (i.e. H or Li) that are hard to find by X-ray diffraction methods by examining the valences of the surrounding atoms.
3. To predict bond distances, as an alternative to ionic radii. This can be done by inverting the equation:

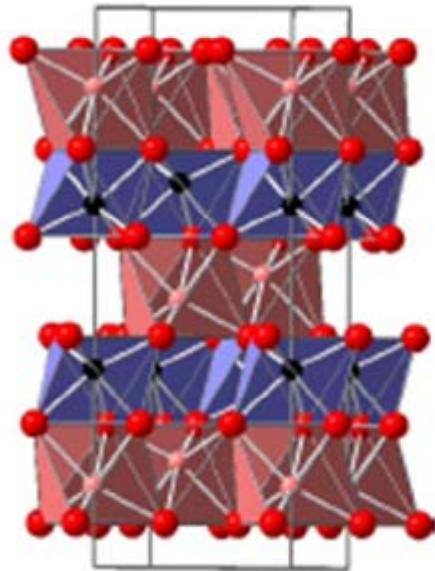
$$d_{ij} = R_{ij} - b\{\ln(s_{ij})\}$$

Advantages over ionic radii include

- Independent of coordination number.
- Can handle unsymmetrical coordination environments.

# Bond Valences & Structural Analysis

## FeTiO<sub>3</sub> (Ilmenite)



铁钛矿

### Bond Distances

$$\text{Fe-O} = 3 \times 2.07, 3 \times 2.20$$

$$\text{Ti-O} = 3 \times 1.88, 3 \times 2.09$$

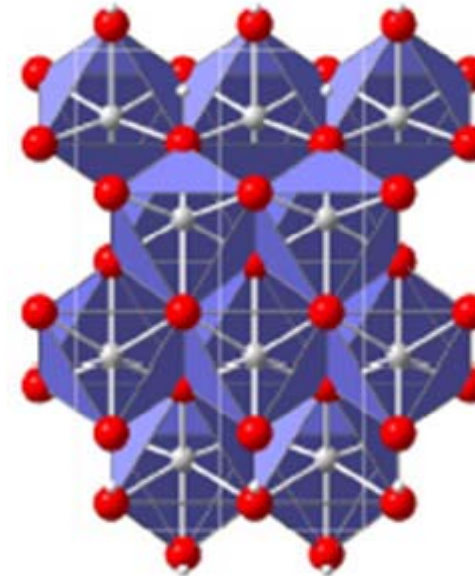
### Bond Valence Sums

$$\text{Fe} = 3 \times 0.40 + 3 \times 0.28 = 2.04$$

$$\text{Ti} = 3 \times 0.84 + 3 \times 0.48 = 3.96$$

$$\text{O} = 0.40 + 0.28 + 0.84 + 0.48 = 2.00$$

## AlOOH (Diaspore)



硬水铝石

### Bond Distances

$$\text{O1-Al} = 1.85, 1.85, 1.86$$

$$\text{O2-Al} = 1.97, 1.97, 1.98$$

### Bond Valence Sums

$$\text{Al} = 2.75$$

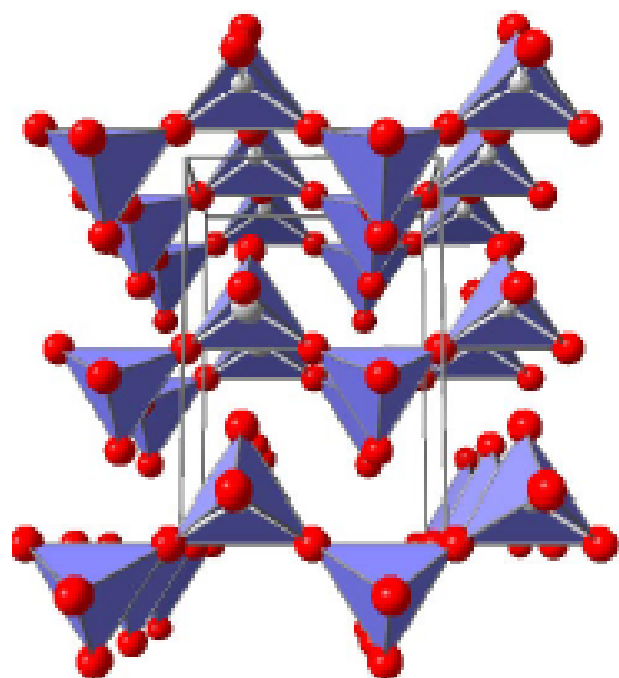
$$\text{O1} = 1.60$$

$$\text{O2} = 1.16$$

← OH

$$R_{\text{Fe-O}} = 1.734, b = 0.37 \rightarrow s_{\text{Fe-O}} = \exp((1.734 - 2.07) / 0.37) = 0.40$$

# Bond Valences Predictively



Two types of Oxide ions -

- Bridging -  $\text{II O}$
- Terminal -  $\text{I O}$

Pauling's 2<sup>nd</sup> rule gives the expected bond valences

- $\text{Cr-II O} \rightarrow s_{ij} = 1.0$
- $\text{Cr-I O} \rightarrow s_{ij} = 2.0$

Inverting the bond valence calculation we can estimate distances

- $\text{Cr-II O} \rightarrow 1.79 \text{ \AA}$
- $\text{Cr-I O} \rightarrow 1.54 \text{ \AA}$

The observed bond distances are

- $\text{Cr-II O} \rightarrow 1.75 \text{ \AA}$
- $\text{Cr-I O} \rightarrow 1.57 \text{ \AA}$



# Bond Valences Predictively

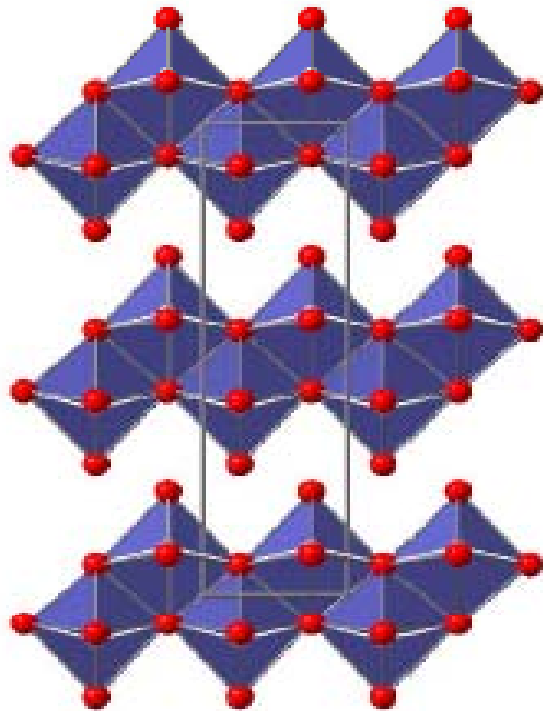
## $\alpha$ - $\text{MoO}_3$

Space Group =  $P-1$

Chains of edge-sharing octahedra

Mo-O Bond distances =

1.67, 1.73, 1.95, 1.95, 2.25, 2.33



## $\beta$ - $\text{MoO}_3$

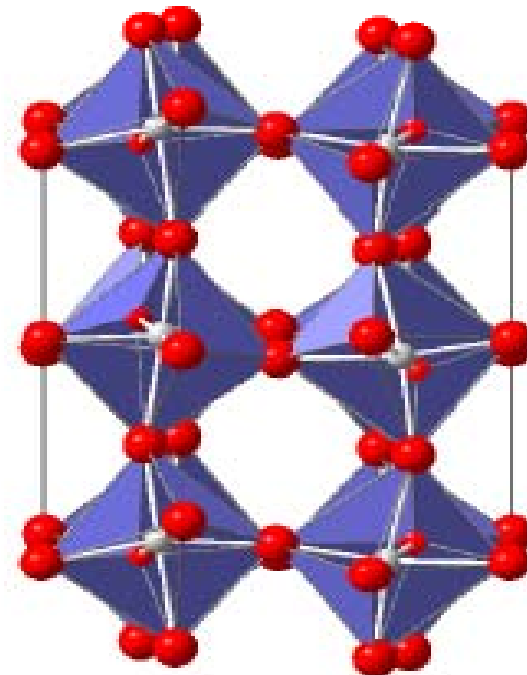
Sp. Group =  $P2_1/n$

Corner sharing octahedra

Mo-O Bond distances =

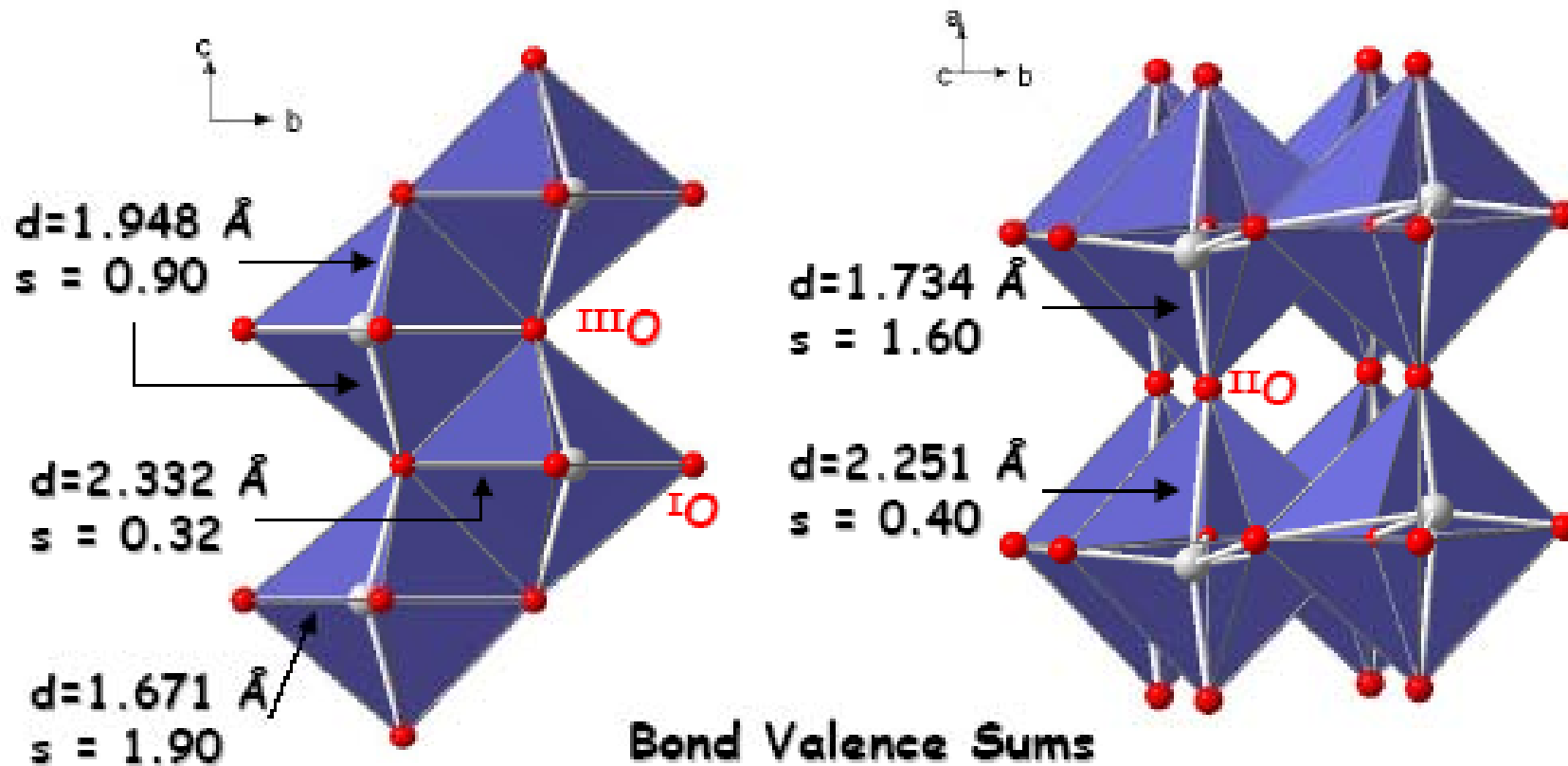
Mo(1) 1.65, 1.79, 1.81, 2.09, 2.12, 2.20

Mo(2) 1.80, 1.87, 1.91, 1.92, 2.01, 2.23



# $\alpha$ -MoO<sub>3</sub> A closer look

The Mo<sup>6+</sup> ions shift away from the shared edges.



## Bond Valence Sums

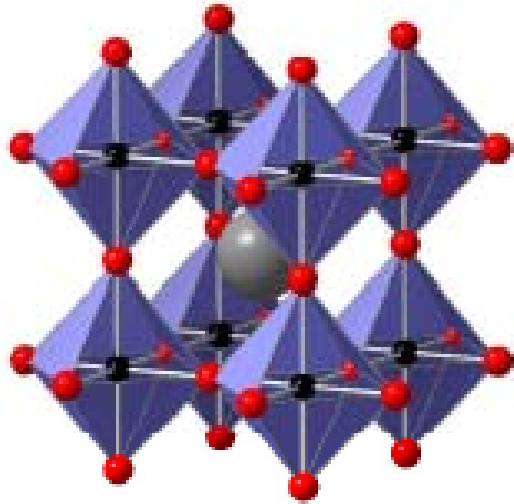
$$\text{Mo} = 2 \times 0.90 + 1.90 + 0.32 + 1.60 + 0.40 = 6.02$$

$$\text{I O} = 1.90$$

$$\text{II O} = 1.60 + 0.40 = 2.00$$

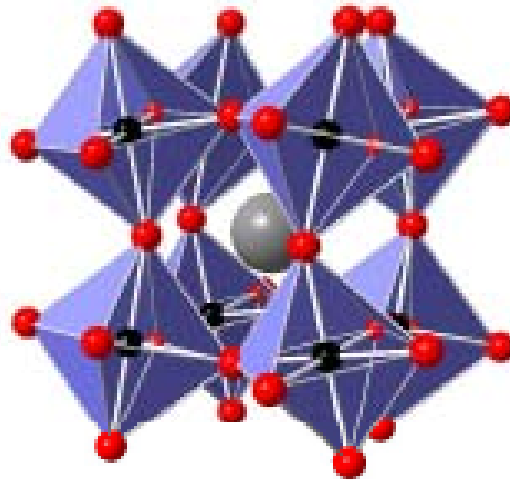
$$\text{III O} = 0.90 + 0.90 + 0.32 = 2.12$$

# Distorted Coordination Environments



**SrTiO<sub>3</sub>**

计算: 3.933 Å; 实际: 3.905 Å



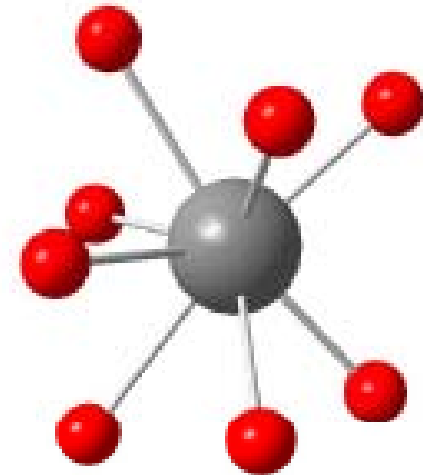
**CaTiO<sub>3</sub>**

How far should the tilting go?

Can you tell from the ionic radii of Ca<sup>2+</sup> and O<sup>2-</sup>?

Ca<sup>2+</sup> (CN=12)  $r = 1.48 \text{ \AA}$   
 Ca<sup>2+</sup> (CN=8)  $r = 1.26 \text{ \AA}$   
 Ca<sup>2+</sup> (CN=6)  $r = 1.14 \text{ \AA}$

O<sup>2-</sup> (CN = 2)  $r = 1.21 \text{ \AA}$   
 O<sup>2-</sup> (CN = 6)  $r = 1.26 \text{ \AA}$

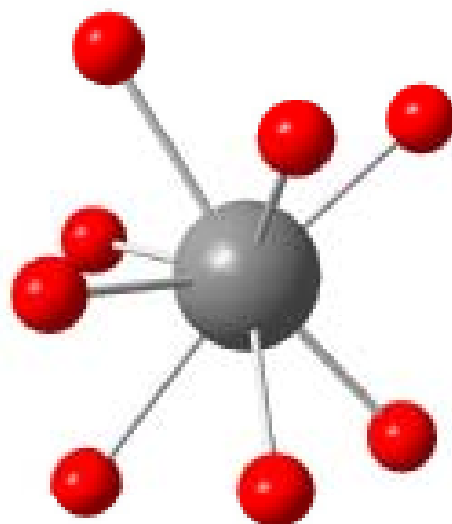


**Ca-O Distances**

1 × 2.36 Å  
 2 × 2.37 Å  
 1 × 2.46 Å  
 2 × 2.62 Å  
 2 × 2.65 Å  
 4 > 3.0 Å

$$R_{\text{Ca-O}} = 1.967, b = 0.37 \rightarrow s_{\text{Ca-O}} = \exp((1.967 - 3.0) / 0.37) = 0.06$$

# Distorted Coordination Environments



## Ca-O Distances

1 × 2.36 Å  
2 × 2.37 Å  
1 × 2.46 Å  
2 × 2.62 Å  
2 × 2.65 Å

## Ca-O Valences

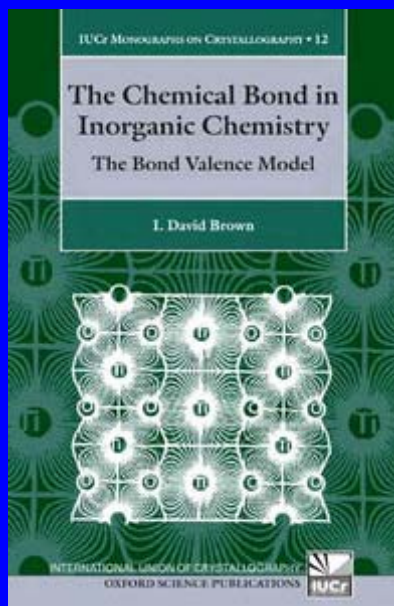
1 × 0.345  
2 × 0.336  
1 × 0.264  
2 × 0.171  
2 × 0.157  

---

V<sub>Ca</sub> = 1.94

# References

- I.D. Brown, “The Chemical Bond in Inorganic Chemistry”.



- I.D. Brown, “Recent developments in the methods and applications of the bond valence model”, Chem Rev. 2009 Dec;109(12):6858-919

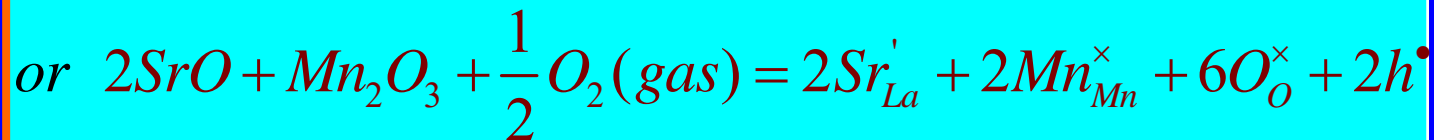
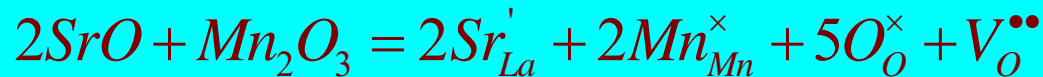
# ABO<sub>3</sub> 的异价掺杂缺陷反应:

A-位低价掺杂, 如  $\text{LaMnO}_3 \rightarrow \text{La}_{1-x}\text{Sr}_x\text{MnO}_3$

整比(3-3型) LMO<sub>3</sub> (ABO<sub>3</sub>)合成反应:



A-位Sr掺杂LMO<sub>3</sub> (ABO<sub>3</sub>)的缺陷反应:



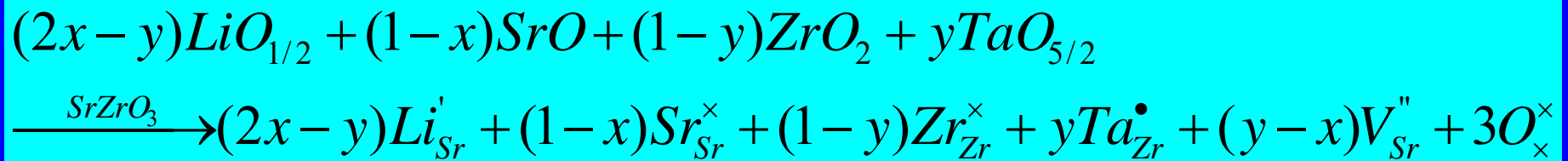
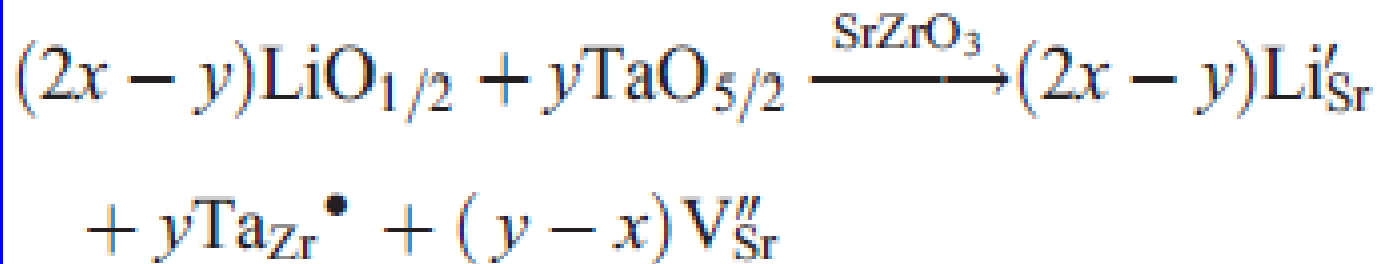
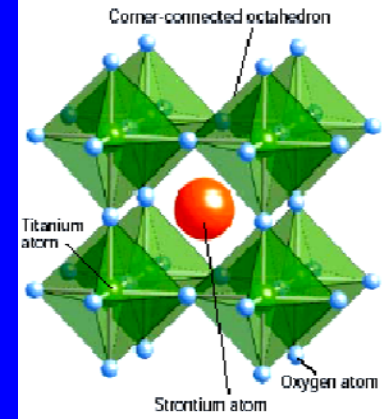
Sr is an  
acceptor  
dopant

A-位高价掺杂, 如  $\text{SrTiO}_3 \rightarrow \text{Sr}_{1-x}\text{La}_x\text{TiO}_3$

La is a donor dopant.



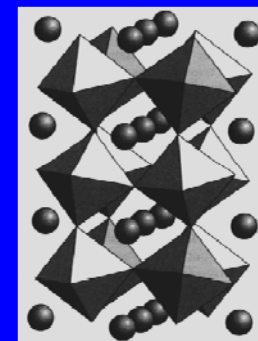
➤ ABO<sub>3</sub> 的A-、B-位异价掺杂缺陷反应：



Similarly,  $\text{LiSrZrNbO}_3$ ,  $\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3$ , ...

Nernst-Einstein 方程：

$$\sigma = D \frac{nq^2}{kT}$$



# 锂电电极材料的晶体结构

三个代表:

①  $\text{LiCoO}_2$ : 层状含锂金属氧化物

e.g.  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , Li-rich,  
 $\text{Li}_2\text{MnO}_3$

②  $\text{LiMn}_2\text{O}_4$ : 尖晶石型锂氧化物

e.g.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$

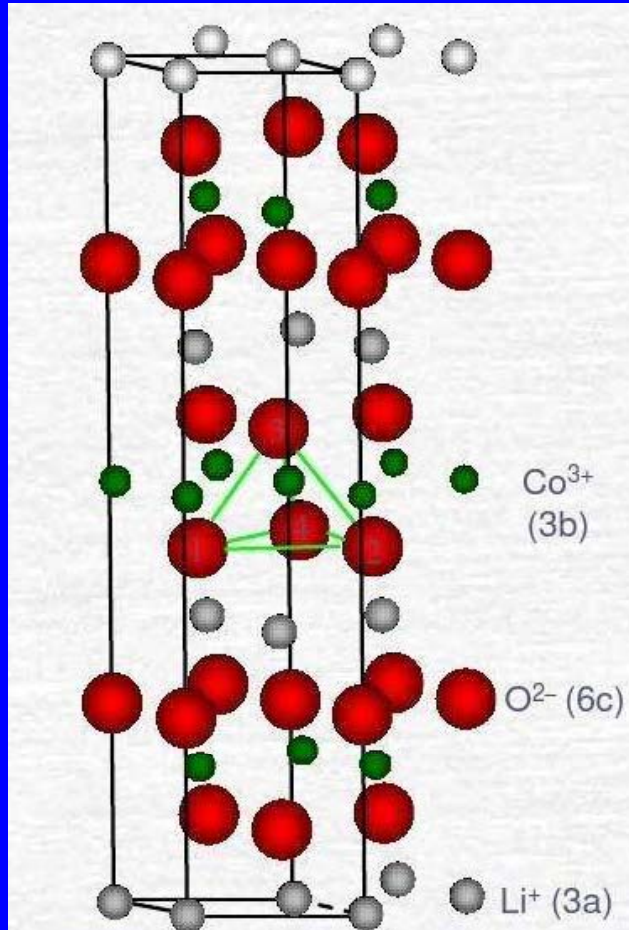
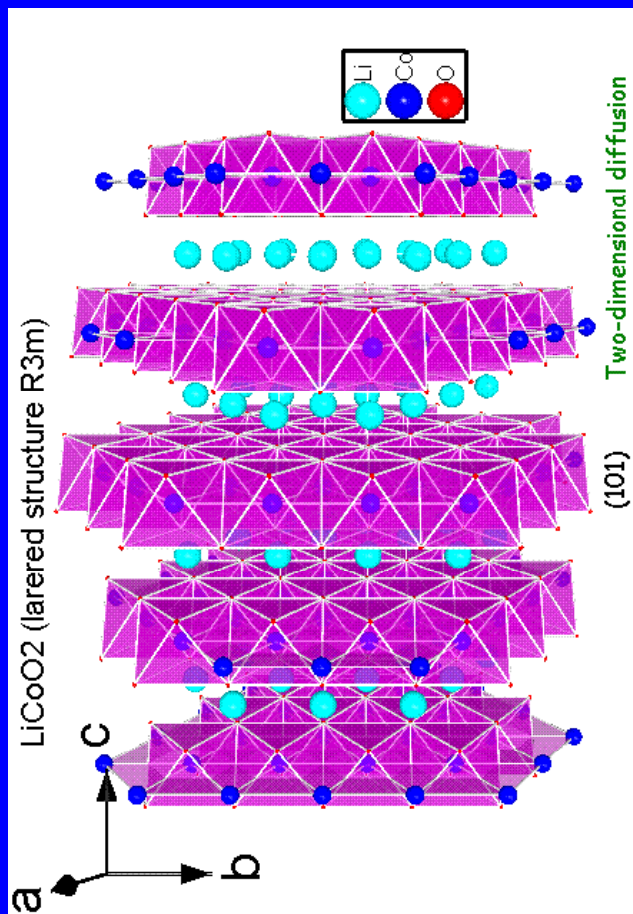
③  $\text{LiFePO}_4$ : 橄榄石结构化合物

e.g.  $\text{LiMnPO}_4$ ,  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ ,

# 锂电电极材料的晶体结构

## ① $\text{LiCoO}_2$ : 层状含锂金属氧化物

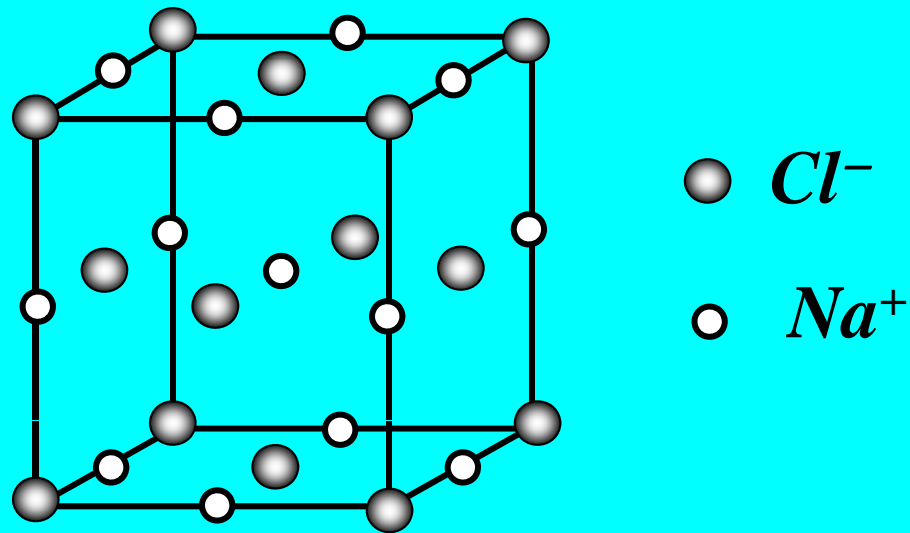
e.g.  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ ,  $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ , Li-rich,  
 $\text{Li}_2\text{MnO}_3$



$\text{LiCoO}_2$ 具有 $\alpha\text{-NaFeO}_2$ 结构, 属六方晶系,  
 $R\text{-}3m$ 空间群, 其中6c位上的O为立方密堆积, 3a  
位的Li和3b位的Co分别交替占据其八面体孔隙,  
在[111]晶面方向上呈层状排列, 理论容量为274  
mAh/g。

# 锂电电极材料的晶体结构

岩盐 (NaCl) 结构:

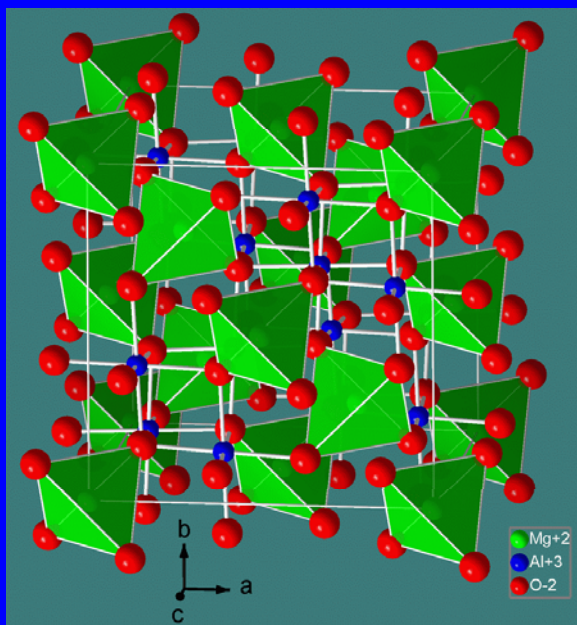


Anions-*fcc*, all **O** occupied and all **T** (T<sup>+</sup> and T<sup>-</sup>) empty.

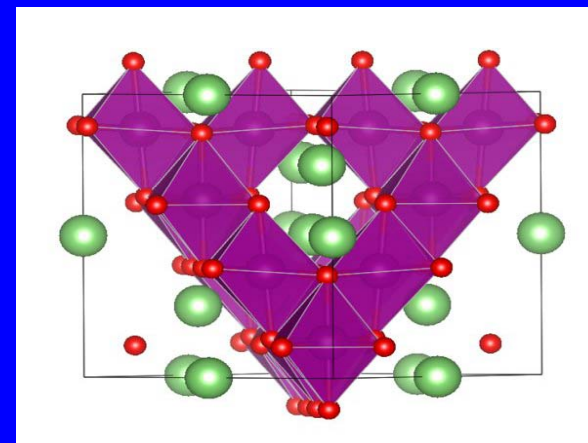
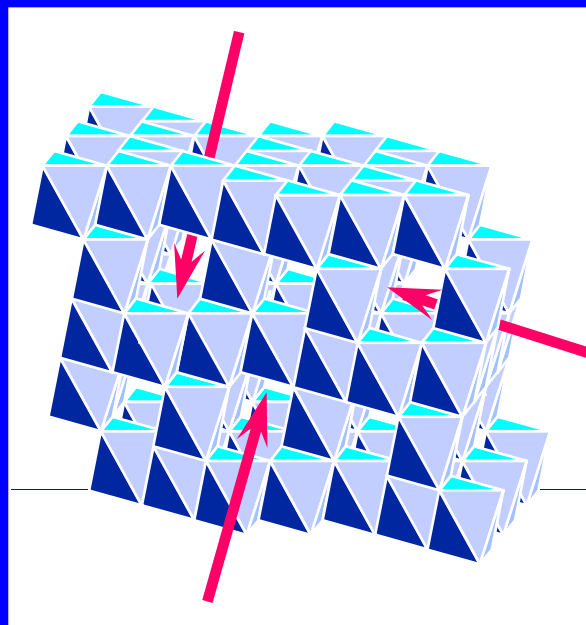
# 锂电电极材料的晶体结构

②  $\text{LiMn}_2\text{O}_4$ : 尖晶石型锂氧化物

e.g.  $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$



$\text{MgAl}_2\text{O}_4$

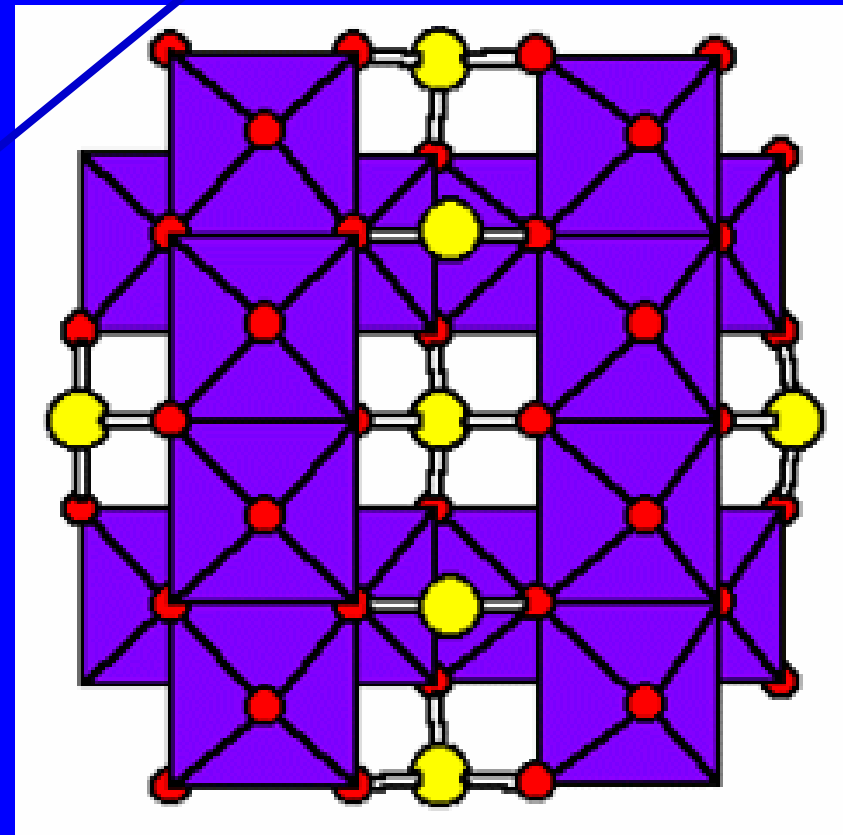
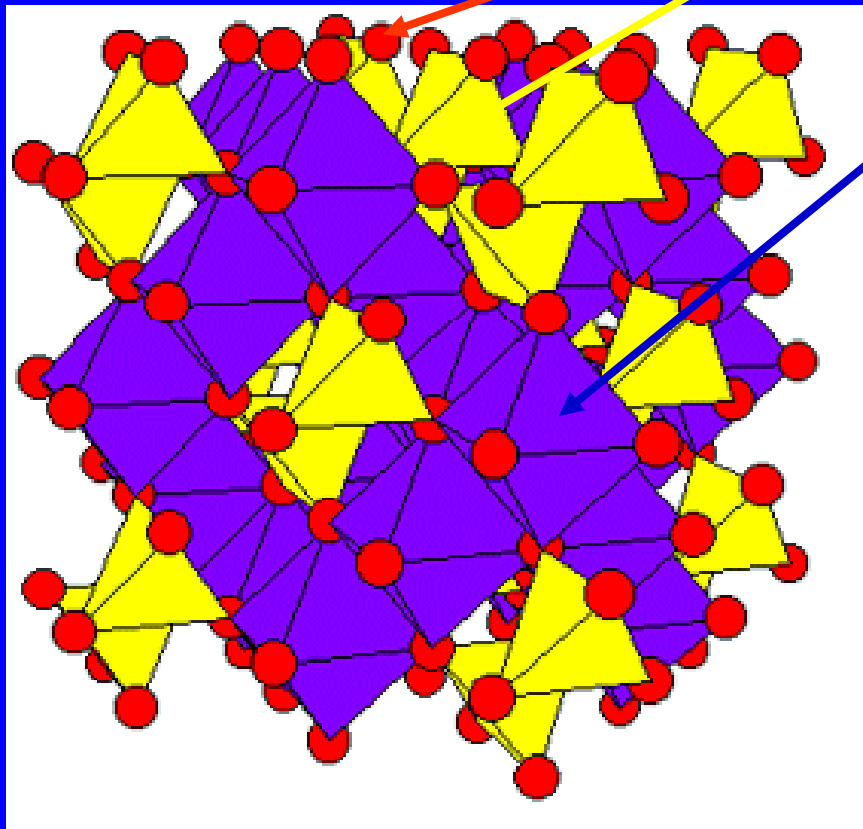


$\text{LiMn}_2\text{O}_4$

# 锂电电极材料的晶体结构

## ② $\text{LiMn}_2\text{O}_4$ : 尖晶石型锂氧化物

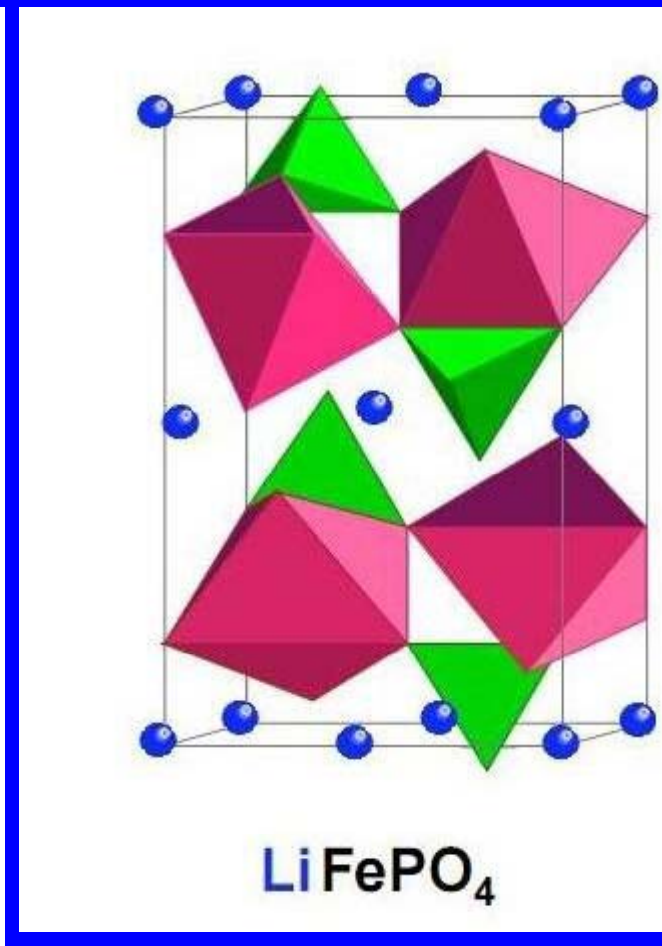
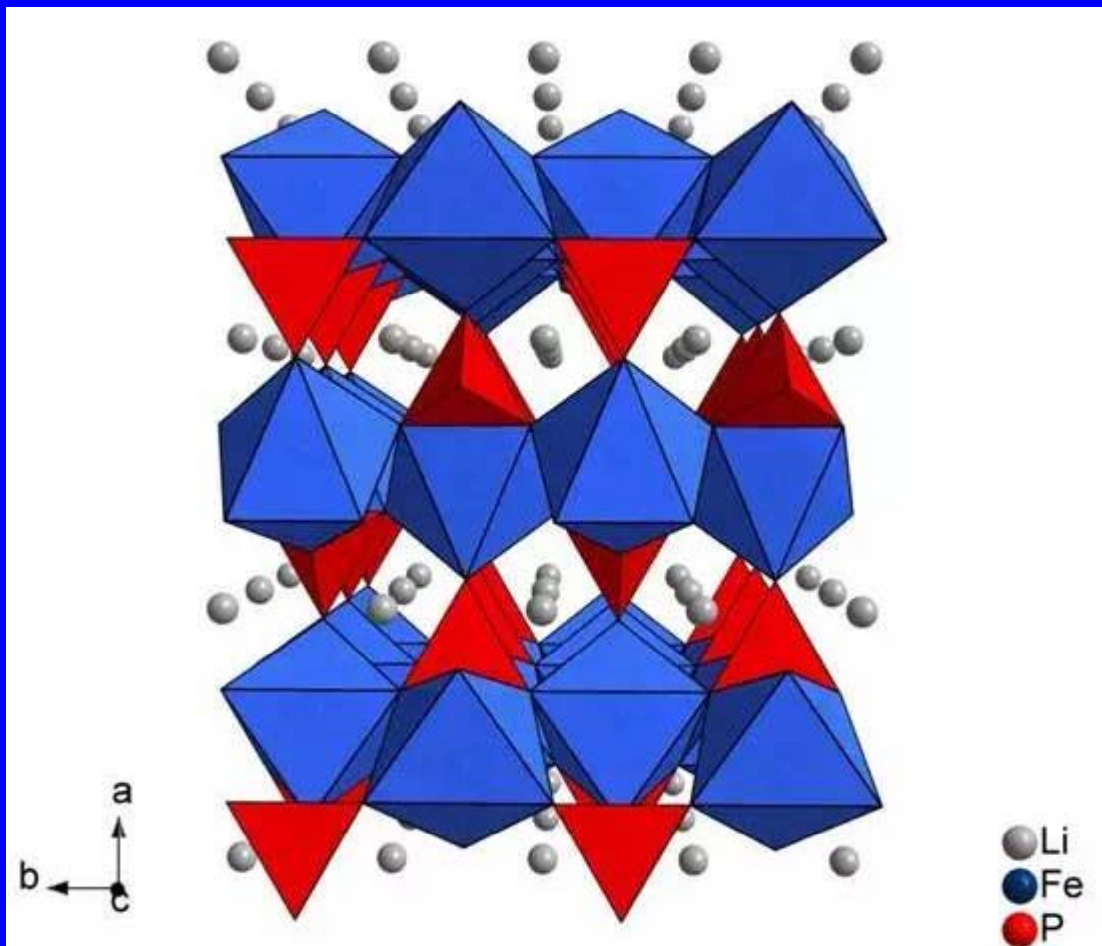
ccp  $\text{O}^{2-}$ ,  $\text{Li}^+$  1/8 Td,  $\text{Mn}^{3+/4+}$  1/2 Oh



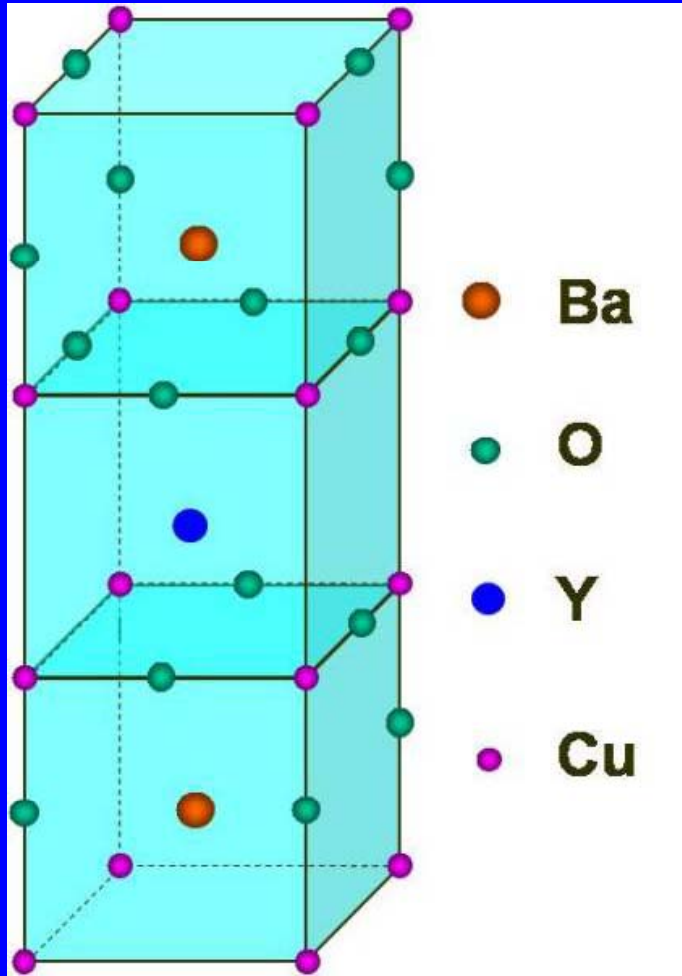


## 锂电电极材料的晶体结构

③  $\text{LiFePO}_4$ : 橄榄石(olivine)结构化合物( $(\text{Mg}^{2+}, \text{Fe}^{2+})_2\text{SiO}_4$ )  
e.g.  $\text{LiMnPO}_4$ ,  $\text{LiFe}_x\text{Mn}_{1-x}\text{PO}_4$ ,



# 高温超导相 $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ 的晶体结构



二氧化锡是n-型还是p-型半导体？

ZnO呢？ CoO呢？

NbO和Nb<sub>2</sub>O<sub>5</sub>呢？

YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub>呢？