

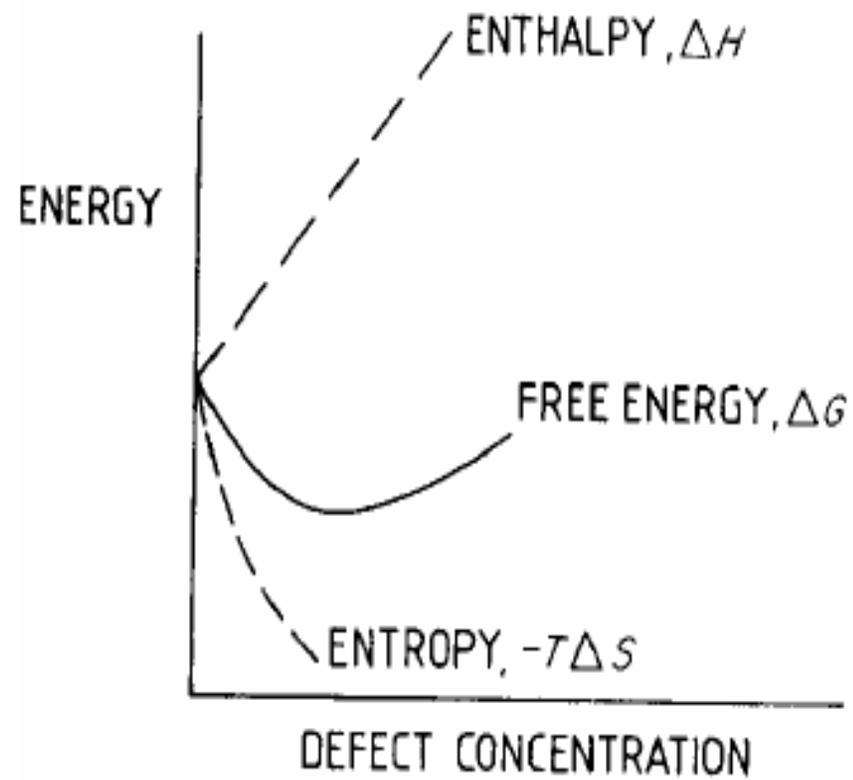
Defeitos em Cristais Iônicos

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Defeitos

- Os defeitos perturbam a ordem a longa distância da rede cristalina e afetam as propriedades dos compostos cristalinos que dependem do volume, *bulk*, como por exemplo a condutividade iônica e a densidade volumétrica . A formação de defeitos é favorecido pelo aumento da Entropia do sistema, entretanto a formação de defeitos é desfavorável do ponto de vista da Entalpia, $\Delta H > 0$. O resultado líquido é que a concentração deles será tão menor quanto menor for a temperatura. O que nos leva a frase:
- Apenas em cristais ideais no zero absoluto não existem defeitos num cristal.

Defeitos



Causas

- Defeitos podem ocorrer devido a:
 - Formação de compostos não-estequiométricos e soluções sólidas – defeito eletrônico
 - Aumento na Entropia durante a cristalização – defeitos pontuais intrínsecos
 - Balanceamento da carga de impurezas retidas mesmo depois da cristalização – defeitos pontuais extrínsecos
 - Alta concentração de defeitos em compostos não-estequiométricos – defeitos do tipo cluster
 - Superfícies e contornos de grãos – defeitos planares

Defeitos Pontuais

- Tipos de Defeitos Pontuais
 - Vacância
 - Átomo intersticial
 - Átomo substitucional
 - Impureza
 - Centro Associado
- Notação de Kroger-Vink
 - Defeito **A** com carga efetiva **b** ocupando um sítio cristalino **a**
 - A_a^b para vacâncias V_a^b

Mapa de Defeitos Pontuais

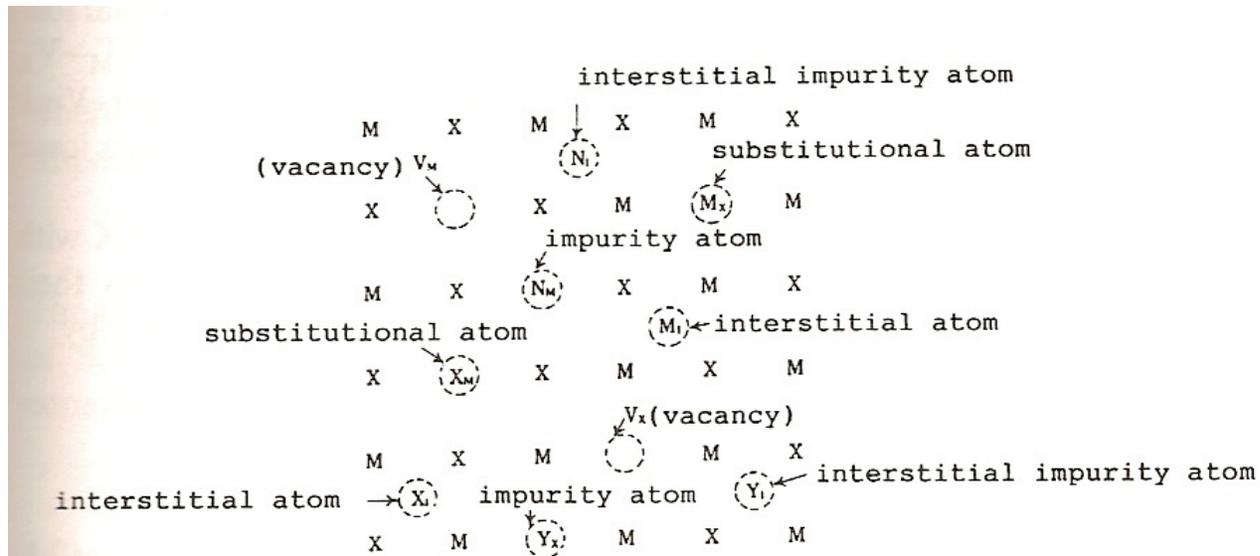


Fig. 2.46 Basic point defects of a MX crystal

Surfaces and grain boundaries are planes where the three-dimensional regularity of a crystal is interrupted. Thus they can also be viewed as (planar) defects.

Defeitos Pontuais

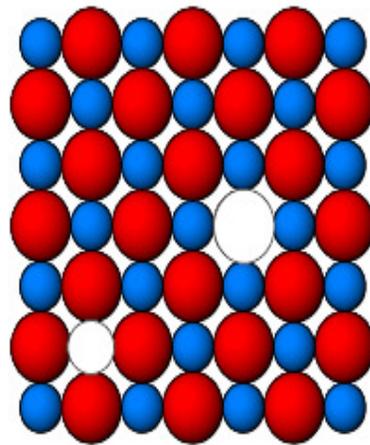
- Vacâncias e átomos intersticiais são partículas que podem ocupar sítios na rede cristalina e possuem carga.
- Sítios são posições no cristal que podem ser ocupadas por átomos do composto, átomos intersticiais e vacâncias. Num composto binário AB nos temos
 - A_A e B_B são o átomo A e o átomo B ocupando seus respectivos sítios na rede e V_A e V_B são vacâncias nos sítios de átomo A e B respectivamente. A_i e B_i são os átomos nos interstício do átomo A e B respectivamente.
 - **Um cristal perfeito é cheio de vacâncias!!!**

O caso do NaCl com impurezas de Ca^{2+}

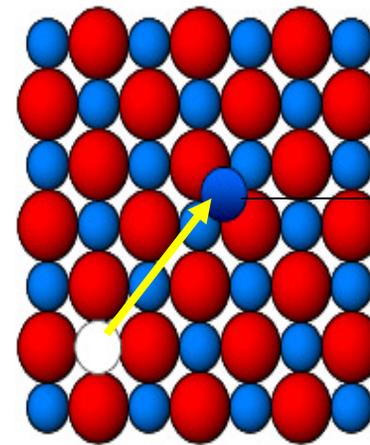
	A átomo (Na^+)	B átomo (Cl^-)	Vacância	C átomo (Ca^{2+})
A- sitio	Na_{Na}	$\text{Cl}^{\prime\prime}_{\text{Na}}$	V^{\prime}_{Na}	$\text{Ca}^{\cdot}_{\text{Na}}$
B- sitio	$\text{Na}^{\cdot\cdot}_{\text{Cl}}$	Cl_{Cl}	V^{\cdot}_{Cl}	$\text{Ca}^{\cdot\cdot\cdot}_{\text{Cl}}$
i- sitio	$\text{Na}^{\cdot}_{\text{i}}$	$\text{Cl}^{\prime}_{\text{i}}$	V_{i}	$\text{Ca}^{\cdot\cdot}_{\text{i}}$

Defeito Schotky e Frenkel

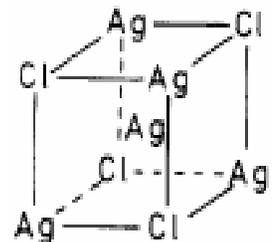
- Presença de vacâncias de cátions e ânions em igual numero = defeito Schotky
- Um íon é deslocado para um espaço intersticial = defeito Frenkel



Schottky Defect
(i.e. NaCl)
 $\text{Na}^+ + \text{Cl}^- \rightarrow V_{\text{Na}} + V_{\text{Cl}}$



Frenkel Defect
(i.e. AgCl)
 $\text{Ag}^+ \rightarrow V_{\text{Ag}^+} \text{Ag}^+_{\text{intersticial}}$



Frequência de Ocorrência de defeitos Schotky e Frenkel

- **Schotky:** estes defeitos são mais comuns e aparecem em maior frequência em compostos com metais que podem apresentar maior número de estados de oxidação. Os haletos de metais alcalinos possuem 10^{-12} mol dm⁻³ de defeitos a 130 °C, enquanto o TiO possui 12 mol dm⁻³ de defeitos Schotky.
- **Frenkel:** defeitos deste tipo não levam a mudança na estequiometria do composto e são encontrados com maior frequência em estruturas mais abertas, por exemplo a esfarelita e a wurtzita, onde o número de coordenação é baixo e a estrutura é menos densa. Defeitos devido a cations são mais comuns que ânions pois os cations são menores. Defeitos com ânions são encontrados em compostos com estrutura tipo fluorita como a zircônia.
- **Defeitos do tipo Frenkel não levam a mudança na densidade volumétrica do composto, enquanto defeitos do tipo Schotky reduzem a densidade do material significativamente.**

Defeito Schotky e Frenkel

Dependência da Temperatura

Em cristais com baixa concentração de vacâncias

$$\frac{N_S}{N} \approx \frac{N_S}{(N - N_S)} = e^{\left\{ -\left(\frac{g_{VM} + g_{VX}}{2kT} \right) \right\}}$$

Onde N_S = qtde de defeitos V_M e V_X ; N = qtidade de sítios na rede de cations e ânions em um mol; g_0 é a energia livre de uma molécula num cristal perfeito e g_{VM} e g_{VX} são as energias livres de formação de V'_M e V'_X .

H.Yanagida et al, The Chemistry of Ceramics, Wiley, 1996, pág. 60-61.

Distribuição de Defeitos

Efeito da Temperatura

Values of n_s/N

T / K	$\Delta H_s = 5 \times 10^{-19} \text{ J}$	$\Delta H_s = 1 \times 10^{-19} \text{ J}$
300	6.12×10^{-27}	5.72×10^{-6}
1000	1.37×10^{-8}	2.67×10^{-2}

Lista de Defeitos Pontuais e as Reações geradoras

Table 2.12 Formation enthalpies of defects (eV)

Compound	Defect reaction	Formation enthalpy	Compound	Defect reaction	Formation enthalpy
NaCl	$\text{null} = V'_{\text{Na}} + V'_{\text{Cl}}$	2.2–2.4	MgO	$\text{null} = V''_{\text{Mg}} + V''_{\text{O}}$	–6
LiF	$\text{null} = V'_{\text{Li}} + V'_{\text{F}}$	2.4–2.7	CaO	$\text{null} = V''_{\text{Ca}} + V''_{\text{O}}$	–6
CaF ₂	$F_{\text{F}}^{\times} = V'_{\text{F}} + F'_{\text{i}}$	2.3–2.8	UO ₂	$O_{\text{O}}^{\times} = V''_{\text{O}} + O''_{\text{i}}$	3.0
	$\text{Ca}_{\text{Ca}}^{\times} = V''_{\text{Ca}} + \text{Ca}''_{\text{i}}$	–7		$U_{\text{U}}^{\times} = V'''_{\text{U}} + U'''_{\text{i}}$	–9.5
	$\text{null} = V''_{\text{Ca}} + 2V'_{\text{F}}$	–5.5		$\text{null} = V'''_{\text{U}} + 2V''_{\text{O}}$	–6.4
BeO	$\text{null} = V''_{\text{Be}} + V''_{\text{O}}$	–6			

Compostos Não-Estequiométricos

- Muitos compostos não podem ser expressos apenas por uma razão única entre cátions e ânions e por isto são chamados de não-estequiométricos. Exemplos destes compostos são os óxidos de metais de transição. Para expressar o desvio da composição estequiométrica usa-se a letra δ . Valores de δ para alguns compostos são dados na Tabela abaixo.

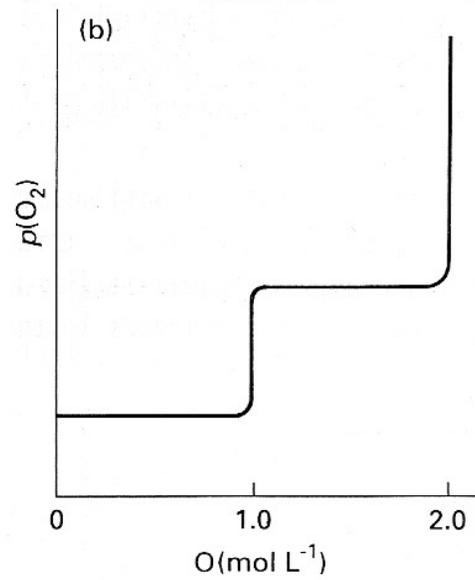
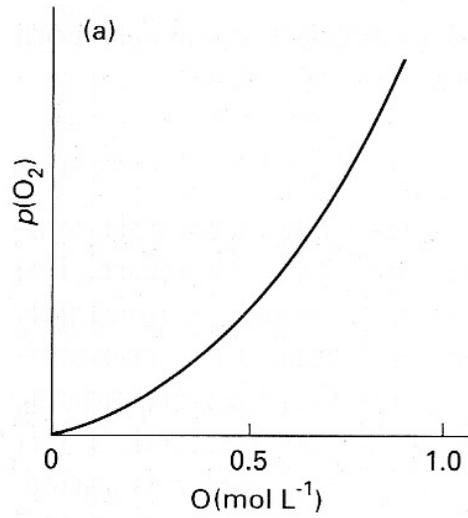
Table 2.13 Deviation from stoichiometry, δ of various non-stoichiometric compounds

Oxide	δ	Oxide	δ
$\text{Fe}_{1-\delta}\text{O}$	0.05–0.15 (1300 K)	$\text{Co}_{1-\delta}\text{O}$	0–0.01
$\text{UO}_{2+\delta}$	0–0.24 (1400 K)	$\text{Ni}_{1-\delta}\text{O}$	0–0.001
$\text{PrO}_{2-\delta}$	0–0.3	$\text{Zn}_{1+\delta}\text{O}$	0– 10^{-6}
$\text{Mn}_{1-\delta}\text{O}$	0–0.1		

Table 18.1 Representative composition rangest of nonstoichiometric binary hydrides, oxides, and sulfides

<i>d</i> block		<i>f</i> block		
Hydrides				
TiH _x	1 to 2		Fluorite type	Hexagonal
ZrH _x	1.5 to 1.6		GdH _x 1.8–2.3	2.85–3.0
HfH _x	1.7 to 1.8		ErH _x 1.95–2.31	2.82–3.0
NbH _x	0.64 to 1.0		LuH _x 1.85–2.23	1.74–3.0
Oxides				
	Rock-salt type	Rutile type		
TiO _x	0.7–1.25	1.9–2.0		
VO _x	0.9–1.20	1.8–2.0		
NbO _x	0.9–1.04			
Sulfides				
ZrS _x	0.9–1.0			
YS _x	0.9–1.0			

†Expressed as the range of values that *x* may take.



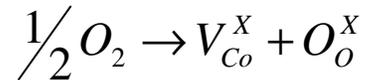
18.5 Schematic representation of the variation of the partial pressure of oxygen with composition at constant temperature for (a) a nonstoichiometric oxide; (b) a stoichiometric pair of metal oxides MO and MO_2 .

Classificação de Compostos não-Estequiométricos

- Deficientes de Cátions: $\text{Cu}_{2-\delta}\text{O}$, $\text{Ni}_{1-\delta}\text{O}$ – vacâncias de cátions
- Com excesso de cátions: $\text{Zn}_{1+\delta}\text{O}$, $\text{Cd}_{1+\delta}\text{O}$; cátions nos interstícios
- Deficientes de ânions: $\text{ZrO}_{2-\delta}$; $\text{PrO}_{2-\delta}$, vacâncias de ânions
- Com excesso de ânions: $\text{UO}_{2-\delta}$ - ânions ocupando interstícios.

Deficientes de Cátions

- $\text{Co}_{1-\delta}\text{O}$:



V_{Co}^{\times} é uma vacância de Co com carga 2+

O_0^{\times} é um ion oxido no sitio correto

$$V_{\text{Co}}^{\times} = V_{\text{Co}}' + h$$

$$V_{\text{Co}}' = V_{\text{Co}}'' + h$$

$$[V_{\text{Co}}^{\times}] = K_1 P_{\text{O}_2}^{1/2}; [V_{\text{Co}}'] p = K_2 [V_{\text{Co}}^{\times}]; [V_{\text{Co}}''] p = K_3 [V_{\text{Co}}']$$

$$\delta = [V_{\text{Co}}^{\times}] + [V_{\text{Co}}'] + [V_{\text{Co}}'']$$

se V_{Co}' são os defeitos majoritarios então :

$$\delta = p = (K_1 K_2)^{1/2} P_{\text{O}_2}^{1/4}$$

se V_{Co}'' são os defeitos majoritarios então :

$$\delta = p = \left(\frac{K_1 K_2 K_3}{4} \right)^{1/3} P_{\text{O}_2}^{1/6}$$

$$\sigma = p e \mu = \text{condutividade elétrica}$$

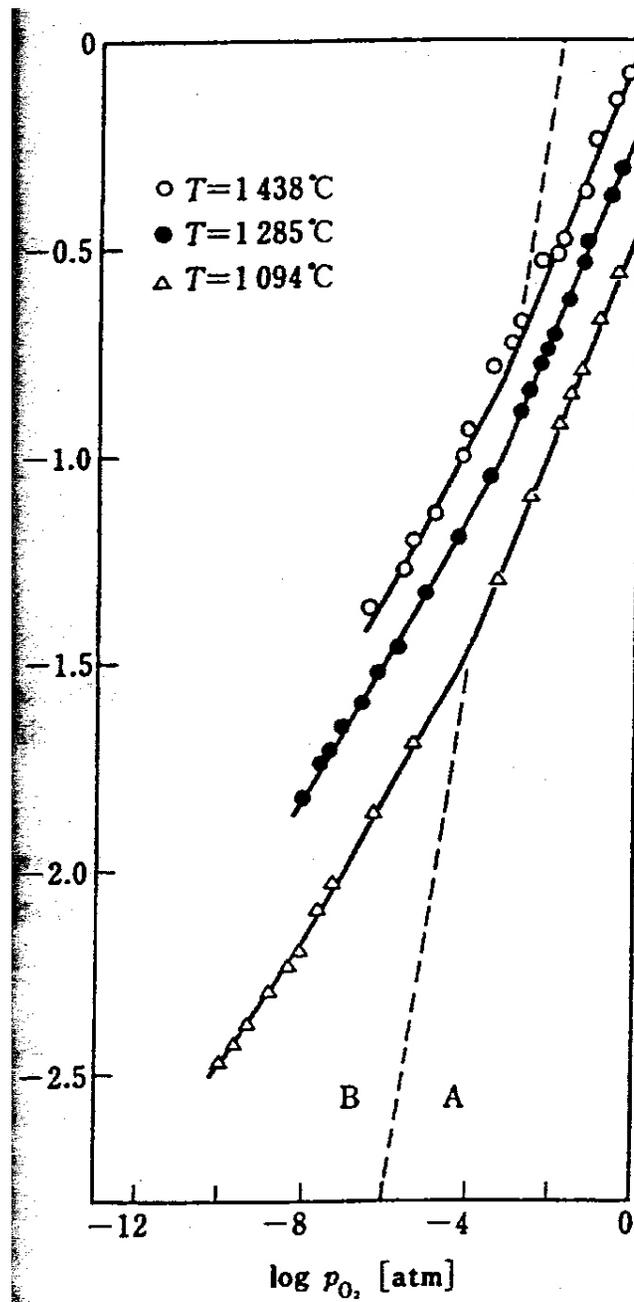


Fig. 2.47 Electrical conductivity versus oxygen partial pressure curves of CoO. (Reproduced by permission of The American Institute of Physics, from B. Fisher and D. S. Tannhauser, *J. Chem. Phys.*, 44, 1663, 1966)

Estrutura de Bandas $\text{Co}_{1-\delta}\text{O}$

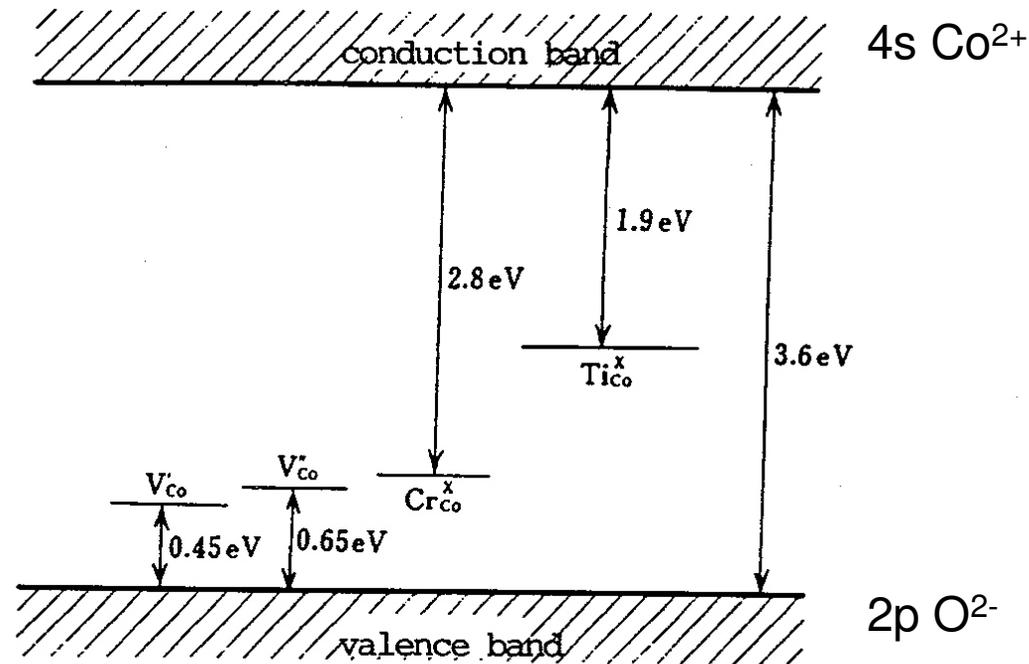
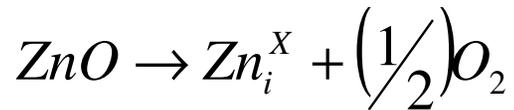


Fig. 2.48 Band structure of CoO . (Reprinted from M. Gvishi and D. S. Tannhauser, *J. Phys. Chem. Solids*, 33, 893, 1972 with kind permission from Elsevier Science Ltd, The Boulevard, Langford Lane, Kidlington OX5 1GB, UK)

CoO é um semiconductor do tipo p e sua condutividade elétrica aumentam com a temperatura e P_{O_2} .

Excesso de Cátions ZnO



se Zn_i^{\times} é o defeito majoritario

$$\delta \propto P_{\text{O}_2}^{-1/2}$$

se Zn_i^{\cdot} é o defeito majoritario

$$\delta \propto n \propto P_{\text{O}_2}^{-1/4}$$

se Zn_i^{\cdot} é o defeito majoritario

$$\delta \propto n \propto P_{\text{O}_2}^{-1/6}$$

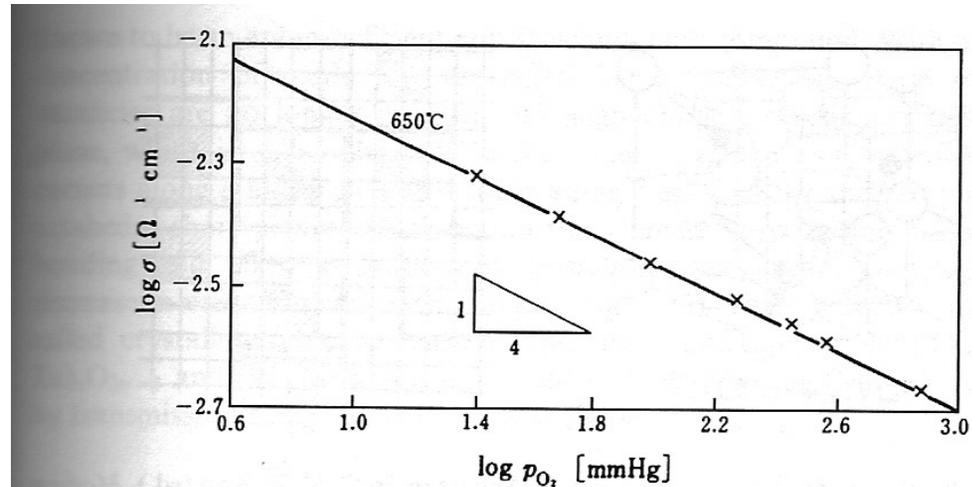


Fig. 2.49 Electrical conductivity versus oxygen partial pressure of ZnO. (From H. H. von Baumbach and C. Wagner, *Z. Phys. Chem.*, B22, 199, 1933. Reproduced by permission of R. Oldenbourg Verlag GmbH)

$$\sigma \propto n \propto P_{\text{O}_2}^{-1/6}$$

então os portadores majoritarios são Zn_i^{\cdot}

Estrutura de Banda do ZnO

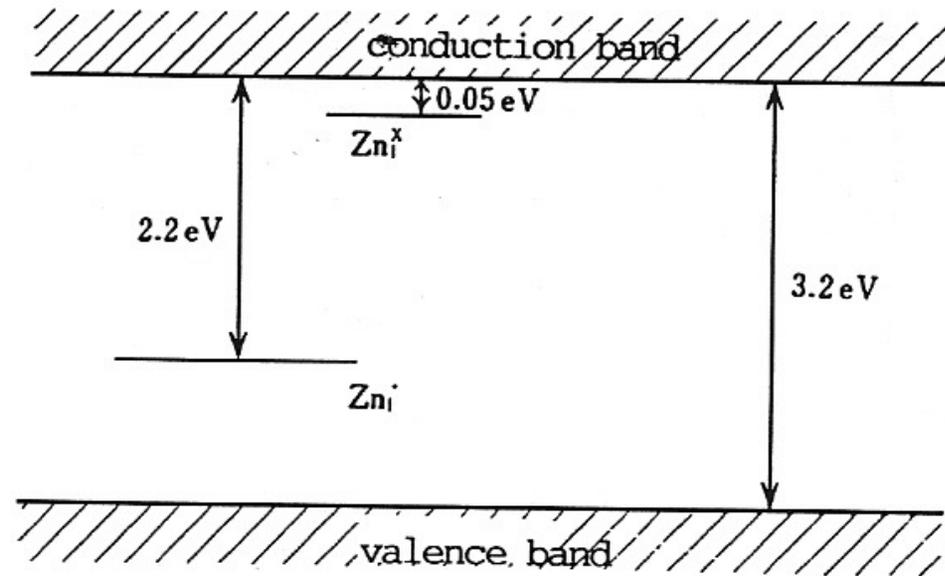


Fig. 2.50 Band structure of ZnO. (From K. Hauffe, *Angew. Chem.*, 72, 730, 1960: reproduced by permission of VCH)

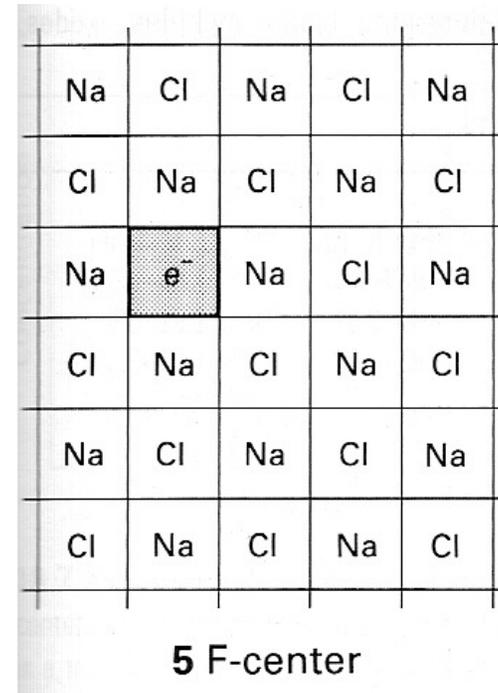
Table 2.14 Valence-controlled semiconductors

Crystal	Additive	Lattice defects formed	Ionic radius Å	Semi-conductor type	Notes
NiO	Li ₂ O	Li' _{Ni} , Ni' _{Ni}	Li ⁺ (6) = 0.68, Ni ³⁺ (6) = 0.60, Ni ²⁺ (6) = 0.69	<i>p</i>	Narrow d-orbital band or hopping thermistor
CoO	Li ₂ O	Li' _{Co} , Co' _{Co}	Li ⁺ (6) = 0.68, Co ³⁺ (6) = 0.63, Co ²⁺ (6) = 0.72	<i>p</i>	Narrow d-orbital band or hopping thermistor
FeO	Li ₂ O	Li' _{Fe} , Fe' _{Fe}	Li ⁺ (6) = 0.68, Fe ³⁺ (6) = 0.64, Fe ²⁺ (6) = 0.74	<i>p</i>	Narrow d-orbital band or hopping thermistor
MnO	Li ₂ O	Li' _{Mn} , Mn' _{Mn}	Li ⁺ (6) = 0.68, Mn ³⁺ (6) = 0.70, Mn ²⁺ (6) = 0.80	<i>p</i>	Narrow d-orbital band or hopping thermistor
ZnO	Al ₂ O ₃	Al' _{Zn} , Zn' _{Zn}	Al ³⁺ (4) = 0.49, Zn ⁺ (4) = 0.93, Zn ²⁺ (4) = 0.71, (0.49 + 0.93)/2 = 0.71	<i>n</i>	sp ³ anti-bond or O ²⁻ -band
TiO ₂	Ta ₂ O ₅	Ta' _{Ti} , Ti' _{Ti}	Ta ⁵⁺ (6) = 0.68, Ti ⁴⁺ (6) = 0.68, Ti ³⁺ (6) = 0.76	<i>n</i>	
Bi ₂ O ₃	BaO	Ba' _{Bi} , Bi' _{Bi}	Ba ²⁺ (8) = 1.43, Bi ⁴⁺ (8) = 0.85, Bi ³⁺ (8) = 1.00	<i>p</i>	High resistance or narrow band (ZNR varistor component)
Cr ₂ O ₃	MgO	Mg' _{Cr} , Cr' _{Cr}	Mg ²⁺ (6) = 0.66, Cr ⁴⁺ (6) = 0.63, Cr ³⁺ (6) = 0.69	<i>p</i>	
Fe ₂ O ₃	TiO ₂	Ti' _{Fe} , Fe' _{Fe}	Ti ⁴⁺ (6) = 0.68, Fe ³⁺ (6) = 0.64, Fe ²⁺ (6) = 0.74	<i>n</i>	
BaTiO ₃	La ₂ O ₃	La' _{Ba} , Ti' _{Ti}	La ³⁺ (12) = 1.23, Ba ²⁺ (12) = 1.47, Ti ⁴⁺ (6) = 0.68, Ti ³⁺ (6) = 0.76	<i>n</i>	PTC thermistor
BaTiO ₃ LaCrO ₃	Ta ₂ O ₅ SrO	Ta' _{Ti} , Ti' _{Ti} Sr' _{La} , Cr' _{Cr}	Sr ²⁺ (12) = 1.25, La ³⁺ (12) = 1.23, Cr ⁴⁺ (6) = 0.63, Cr ³⁺ (6) = 0.69	<i>n</i> <i>p</i>	PTC thermistor High-temperature heating element
LaMnO ₃	SrO	Sr' _{La} , Mn' _{Mn}	Sr ²⁺ (12) = 1.25, La ³⁺ (12) = 1.23, Mn ⁴⁺ (6) = 0.60, Mn ³⁺ (6) = 0.70	<i>p</i>	High-temperature heating element
K ₂ O·11 Fe ₂ O ₃	TiO ₂	Ti' _{Fe} , Fe' _{Fe}		<i>n</i>	Mixed ion-electron conductor
SnO ₂	Sb ₂ O ₅	Sb' _{Sn} , Sn' _{Sn}	Sb ⁵⁺ (6) = 0.62, Sn ³⁺ (6) = 0.81, Sn ⁴⁺ (6) = 0.71, (0.62 + 0.81)/2 = 0.715	<i>n</i>	Transparent electrode

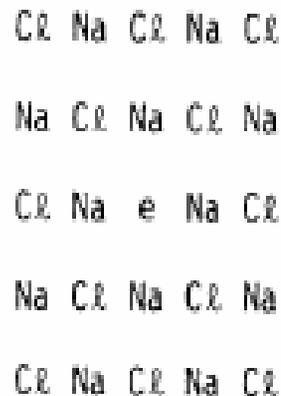
Centros de Cor

centro-F

Centros de cor são originados pelo tratamento dos cristais com radiação ou tratamento com gases fortemente oxidantes como os de metais alcalinos. Estes centros são vacâncias com elétrons aprisionados no poço de potencial feito pela eliminação do ânion. A cor destes centros advém de transições eletrônicas entre os níveis do elétron na caixa.

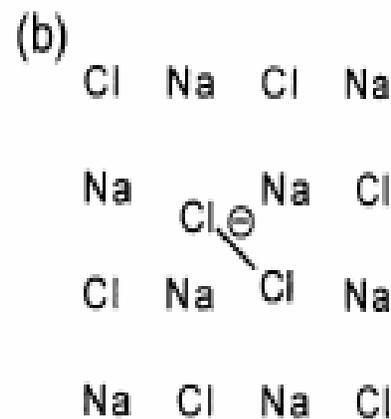
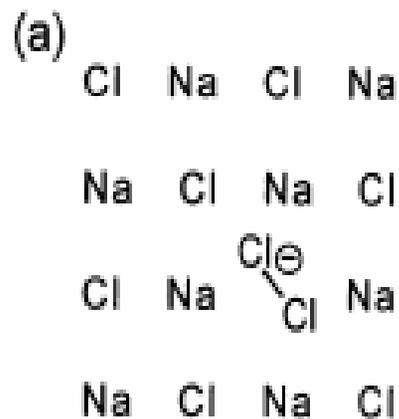


Tipos de centro de Cor



F Center – electron trapped in anion vacancy

Example of color center as trapped electron leads to absorption in visible

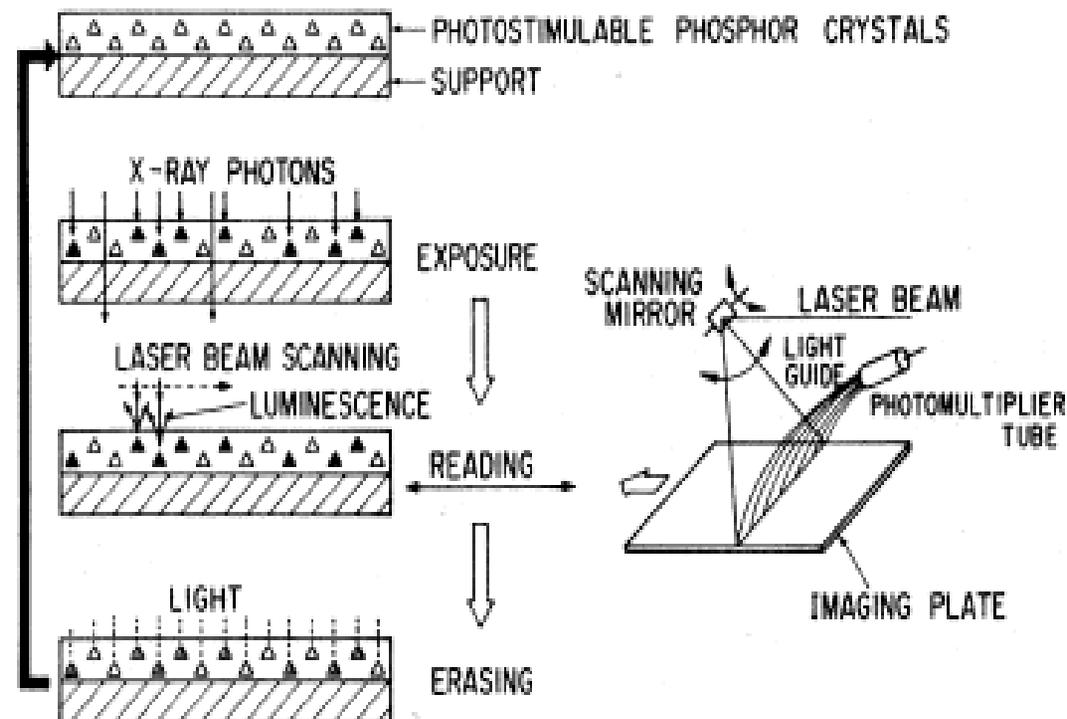


H Center – interstitial Cl atom bonds to lattice Cl⁻

V Center – electron removed from lattice anion site, resulting Cl atom pairs with neighboring Cl⁻

Placas de Imagem

- Color centers are useful in medical X-rays using BaFBr:Eu^{2+} phosphors



Soluções Solidas

Substitutional solid solutions

- ◆ In many compounds it is possible to replace a metal atom or ion with another element that has similar size and bonding requirements
 - In metal alloy can replace metal atom with another element that is within 15% size
 - Can get complete solid solution formation between Al_2O_3 and Cr_2O_3 – $\text{Al}_{2-x}\text{Cr}_x\text{O}_3$
 - Extensive solid solution formation is favored by high temperatures due to the disorder associated with the solid solution

Critérios Solução Sólida

- ◆ Typically, for an ionic solid the ion size difference should be less than 15-20% to get complete solid solution formation
 - > 30% size difference usually precludes solid solution formation
- ◆ End member of solid solution should have same structure if complete solid solutions is to form
 - Zn_2SiO_4 and Mg_2SiO_4 have different metal coordination
 - » So $\text{Zn}_{2-x}\text{Mg}_x\text{SiO}_4$ and $\text{Mg}_{2-x}\text{Zn}_x\text{SiO}_4$ have different structures

Characterizing solid solutions

- ◆ Can determine if solid solution forms by measuring lattice constants of material using x-ray diffraction
 - Lattice constants typically vary linearly with solid solution composition
 - » Vegard's law
- ◆ Can work out mechanism of solid solution formation with the aid of density determination

Deslocamentos

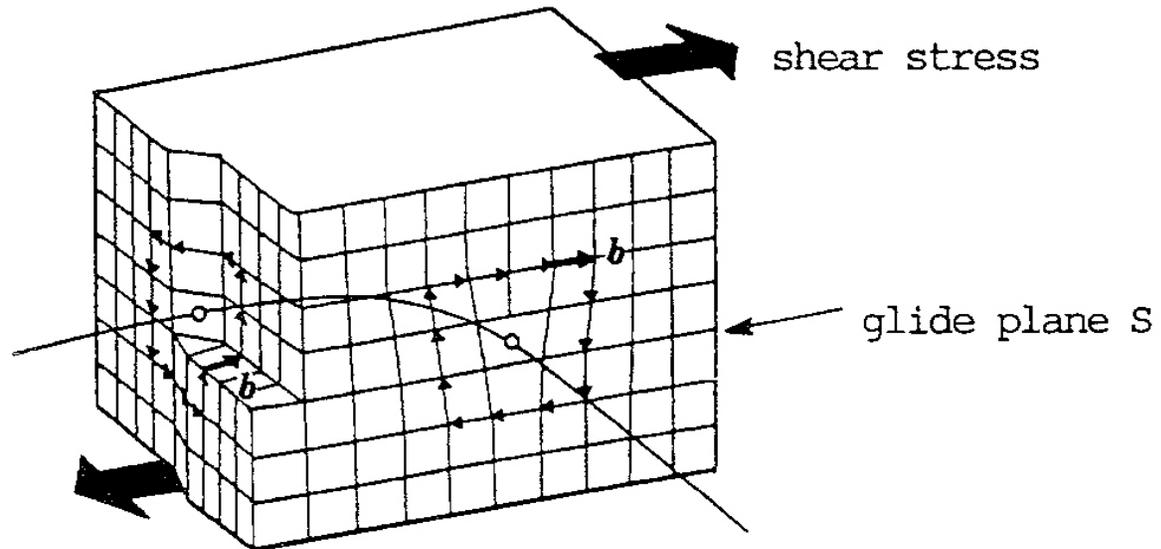


Fig. 2.57 Schematics of dislocations

Cluster de Defeitos

Defeitos pontuais que exibem ordem cristalograficamente a curta distância são chamados de clusters.

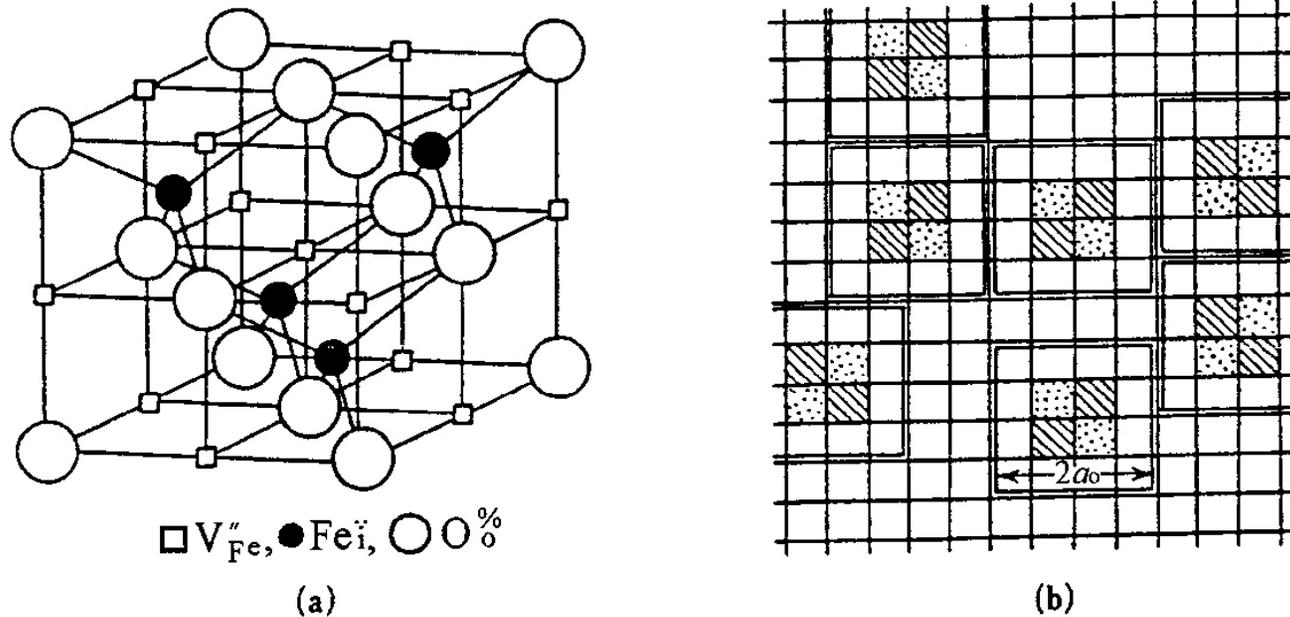
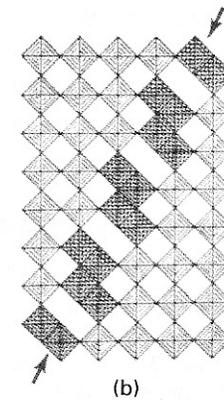
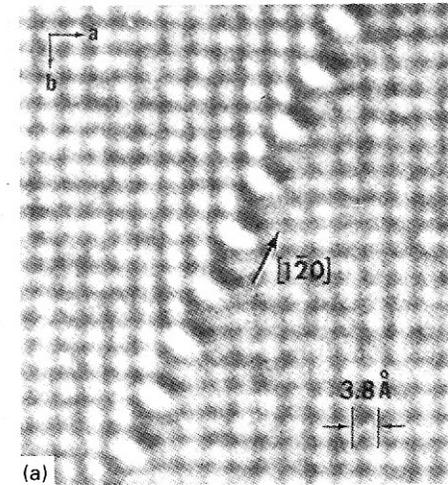
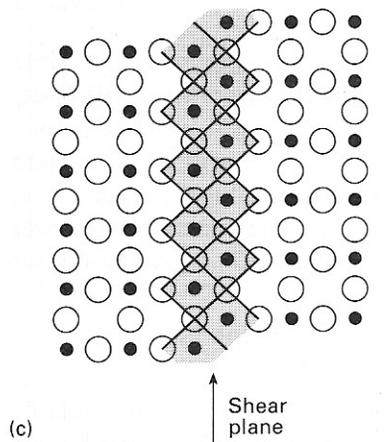
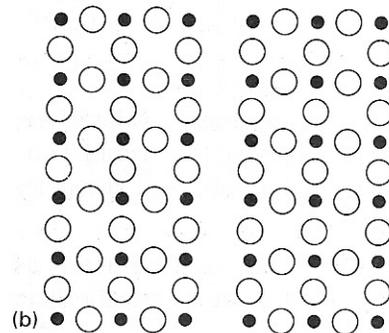
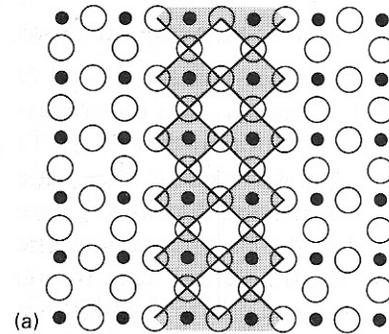


Fig. 2.51 Koch cluster of $Fe_{1-\delta}O$. (From J. S. Anderson, in C. N. R. Rao (ed.), *Modern Aspects of Solid State Chemistry*, Plenum Press, 1970, p. 29: reproduced by permission of Plenum Press)

Planos de Cisalhamento

18.3 The concept of a crystallographic shear plane illustrated by the [100] plane of the ReO_3 structure. (a) A plane of metal, \bullet , and oxygen, \circ , atoms. The octahedron around each metal atom is completed by a plane of O atoms above and below the plane illustrated here. Some of the octahedra are shaded to clarify the processes that follow. (b) Oxygen atoms in the plane perpendicular to the page are removed, leaving two planes of metal atoms that lack their sixth oxygen ligand. (c) The octahedral coordination of the two planes of metal atoms is restored by translating the right slab as shown. This creates a plane (labeled the shear plane) vertical to the paper in which the MO_6 octahedra share edges.



e

Conductividade Iônica e Eletrônica

Factors effecting the conductivity

- $\sigma = n Z e \mu$
- Conductivity is influenced by 1) the carrier concentration n , 2) the carrier mobility μ
- Usually, defects act as the charge carriers
 - not many defects in most ionic solids
 - mobility is usually low at room temperature

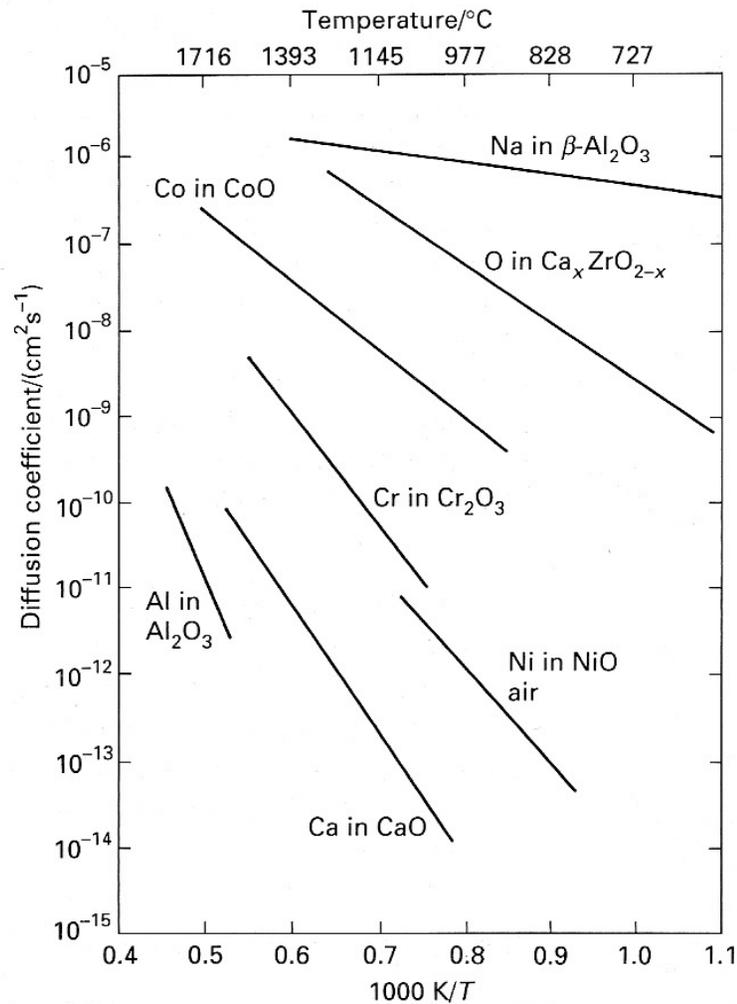
	Material	Conductivity (S m ⁻¹)
Ionic conductors	Ionic crystals	$< 10^{-16} - 10^{-2}$
	Solid Electrolytes	$10^{-1} - 10^3$
	Liquid electrolytes	$10^{-1} - 10^3$
Electronic conductors	Metals	$10^3 - 10^7$
	Semiconductors	$10^{-3} - 10^4$
	Insulators	$< 10^{-10}$

Dependência da Temperatura

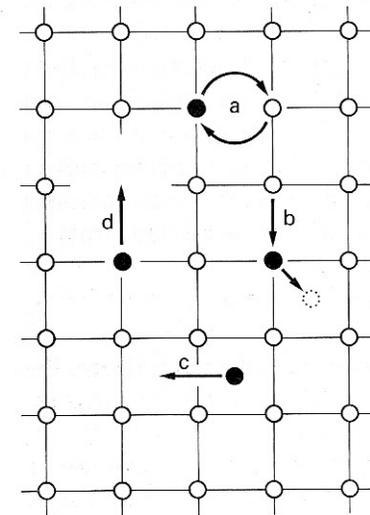
$$\sigma = (\sigma_0/T) \exp(-E_a/kT)$$

- Contribution from mobility and defect formation

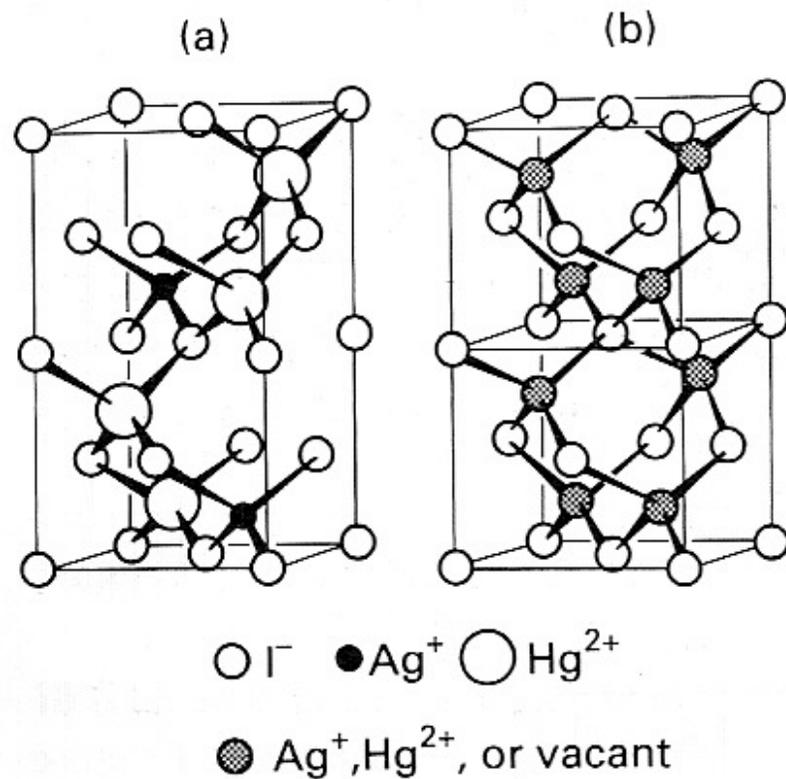
Condutividade Iônica e Eletrônica



18.8 Arrhenius plot of the logarithm of the diffusion coefficient of the mobile ion in a series of solids versus $1/T$.



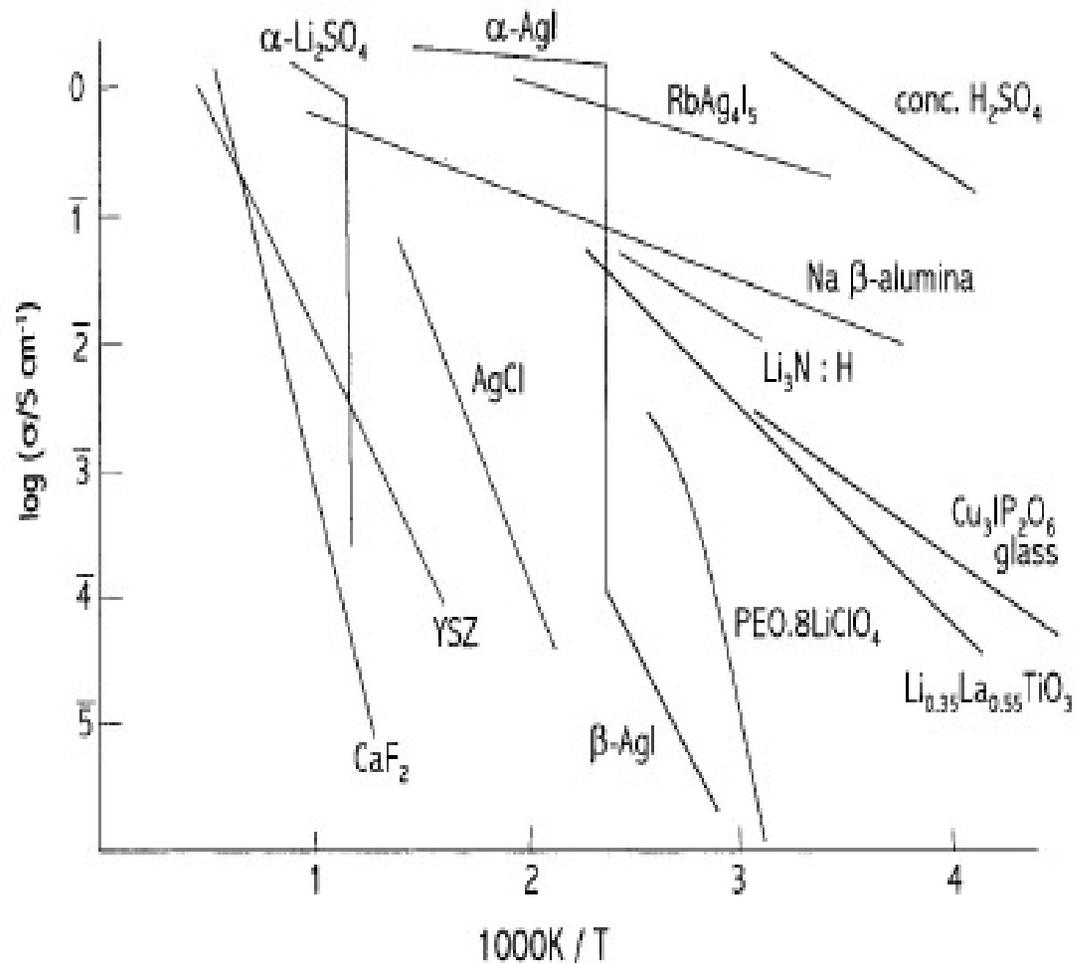
18.9 Some diffusion mechanisms for ions or atoms in a solid: (a) exchange, (b) interstitialcy, (c) interstitial, and (d) vacancy.



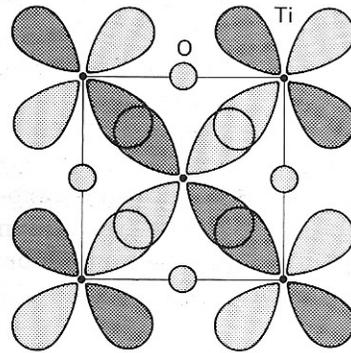
18.10 (a) Low temperature ordered structure of Ag_2HgI_4 . (b) High-temperature disordered structure. Ag_2HgI_4 is an Ag^+ ion conductor in the high temperature form.

- There is a technological need for solids that have very high ionic conductivities
- Such materials are referred to as FAST ION CONDUCTORS
- They include:
 - α AgI
 - Na β alumina
 - NASICON, $\text{Na}_{1+x}\text{Zr}_2[(\text{PO}_4)_{3-x}(\text{SiO}_4)_x]$
 - Stabilized zirconias

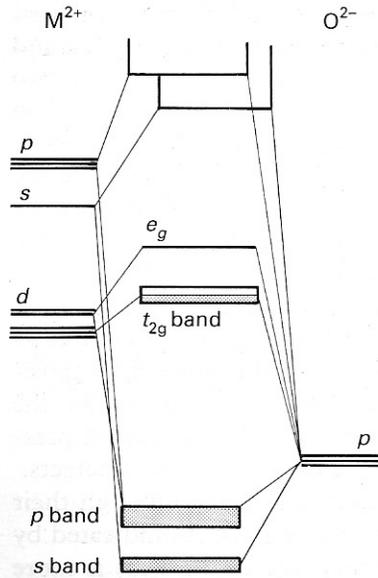
Bons condutores iônicos



Conductividade Eletrônica



18.14 Overlap of d_{xx} orbitals in TiO.



18.15 Energy level diagram for early d -block metal monoxides. The t_{2g} band is only partly filled and metallic conductivity results.

Catálise e Defeitos

Redução de NO a N₂ sobre Perovskita



Pelo Princípio da Eletroneutralidade temos:

$$3 + 2 + 3(1 - x - z) + 2z + 2(x - y) + 3y - 2(4 + \delta) = 0.$$

Então, o número de vacância de íons O²⁻ é dado por :

$$2\delta = -\{(x - y) + z\}$$

Catal Lett (2009) 129:240–246

Efeito do $[V_O]$ na Atividade Catalítica

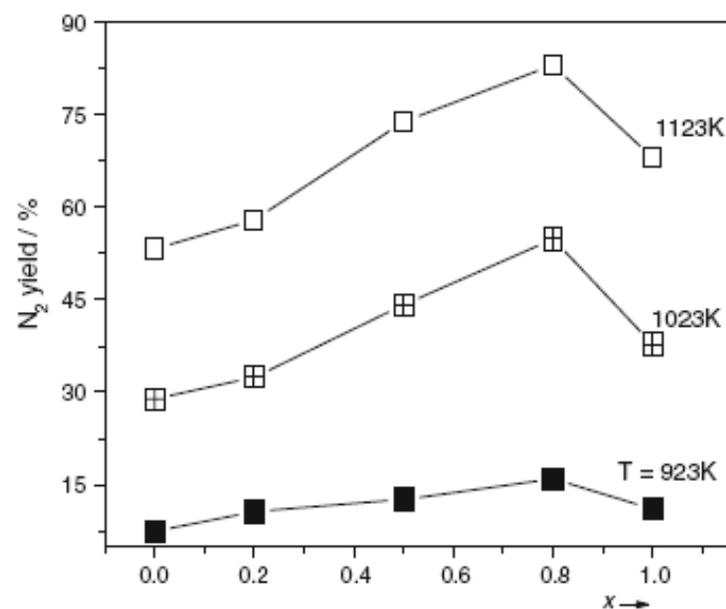
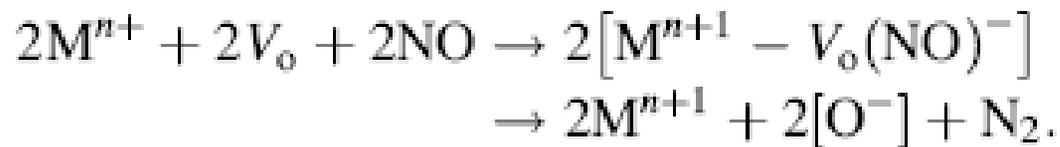


Fig. 5 Activity of NO decomposition measured over $\text{LaSrMn}_{1-x}\text{Ni}_x\text{O}_{4+\delta}$ ($0 \leq x \leq 1$), in the absence of oxygen

Catalysts	BET (m^2/g)	N ₂ yield (%) ^e
$\text{LaSrMnO}_{4+\delta}$	6.72	27.7
$\text{LaSrMn}_{0.8}\text{Ni}_{0.2}\text{O}_{4+\delta}$	7.75	28.0
$\text{LaSrMn}_{0.5}\text{Ni}_{0.5}\text{O}_{4+\delta}$	7.48	48.1
$\text{LaSrMn}_{0.2}\text{Ni}_{0.8}\text{O}_{4+\delta}$	7.42	72.4
$\text{LaSrNiO}_{4+\delta}$	6.46	38.0

Mecanismo de Redução de NO sobre Perovskita Mista

Equação Global



And/or

