

Crystal Physics

Pyroelectricity

Pyroelectricity is described by a rank 1 tensor

$$\pi_i = \frac{\partial P_i}{\partial T}$$

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \begin{bmatrix} \pi_x \\ \pi_y \\ \pi_z \end{bmatrix} = \begin{bmatrix} \pi_x \\ \pi_y \\ -\pi_z \end{bmatrix} \Rightarrow \begin{bmatrix} \pi_x \\ \pi_y \\ 0 \end{bmatrix}$$

rank 1: pyroelectric effect, pyromagnetic effect, electrocaloric effect, magnetocaloric effect

Rank 2 Tensors

Electric susceptibility

Dielectric constant

Magnetic susceptibility

Thermal expansion

Electrical conductivity

Thermal conductivity

Seebeck effect

Peltier effect

Polarization tensor

$$P_i = \chi_{ij} E_j$$

$$\begin{bmatrix} P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} \chi_{xx} & \chi_{xy} & \chi_{xz} \\ \chi_{yx} & \chi_{yy} & \chi_{yz} \\ \chi_{zx} & \chi_{zy} & \chi_{zz} \end{bmatrix} \begin{bmatrix} E_x \\ E_y \\ E_z \end{bmatrix}$$

Transforming P and E by a crystal symmetry must leave the polarization tensor unchanged

$$U\vec{P} = \chi U\vec{E}$$

$$U^{-1}U\vec{P} = U^{-1}\chi U\vec{E}$$

$$\chi = U^{-1}\chi U$$

If rotation by 180 about the z axis is a generating matrix,

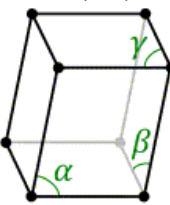
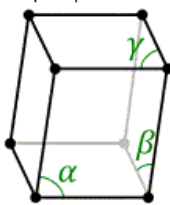
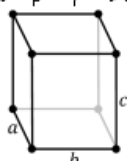
$$U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$U^{-1} = U = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

$$U^{-1}\chi U = \begin{bmatrix} \chi_{xx} & \chi_{xy} & -\chi_{xz} \\ \chi_{yx} & \chi_{yy} & -\chi_{yz} \\ -\chi_{zx} & -\chi_{zy} & \chi_{zz} \end{bmatrix}$$

$$\chi_{xz} = \chi_{yz} = \chi_{zx} = \chi_{zy} = 0$$

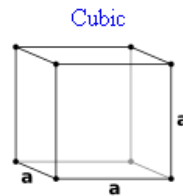
The 32 Crystal Classes

Crystal system	Crystal Class	International symbol	Schoenflies symbol	Space groups	2-fold axes	3-fold axes	4-fold axes	6-fold axes	mirror planes	inversion	Examples	Number of symmetry elements
<p>Triclinic</p> $a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$ 	triclinic-pedial	1	C_1	1	-	-	-	-	-	n		1
	triclinic-pinacoidal	$\bar{1}$	$S_2 = C_i$	2	-	-	-	-	-	y		2
<p>Monoclinic</p> $a \neq b \neq c$ $\alpha \neq 90^\circ$, $\beta = \gamma = 90^\circ$ 	monoclinic-sphenoidal	2	C_2	3-5	1	-	-	-	-	n		2
	monoclinic-domatic	m	$C_{1h} = C_s$	6-9	-	-	-	-	1	n		2
	monoclinic-prismatic	$2/m$	C_{2h}	10-15	1	-	-	-	1	y		4
<p>Orthorhombic</p> $a \neq b \neq c$ $\alpha = \beta = \gamma = 90^\circ$ 	orthorhombic-disphenoidal	222	$V = D_2$	16-24	3	-	-	-	-	n		4
	orthorhombic-pyramidal	$mm2$	C_{2v}	25-46	1	-	-	-	2	n		4
												47: $YBa_2Cu_3O_{7-x}$

Cubic crystals

All second rank tensors of cubic crystals reduce to constants

- 216: ZnS, GaAs, GaP, InAs
- 221: CsCl, cubic perovskite
- 225: Al, Cu, Ni, Ag, Pt, Au, Pb, NaCl
- 227: C, Si, Ge, spinel
- 229: Na, K, Cr, Fe, Nb, Mo, Ta



23	T	195-199		12
$m\bar{3}$	T_h	200-206		24
432	O	207-214		24
$\bar{4}3m$	T_d	215-220	216: Zincblende, ZnS, GaAs, GaP, InAs, SiC	24
$m\bar{3}m$	O_h	221-230	221: CsCl, cubic perovskite 225: fcc, Al, Cu, Ni, Ag, Pt, Au, Pb, γ -Fe, NaCl 227: diamond, C, Si,	48

$$\begin{bmatrix} \xi_{11} & 0 & 0 \\ & \xi_{11} & 0 \\ & & \xi_{11} \end{bmatrix}$$

Rank 3 Tensors

Piezoelectricity

Piezomagnetism

Hall effect

Nerst effect

Ettingshausen effect

Nonlinear electrical
susceptibility

Nonlinear optics

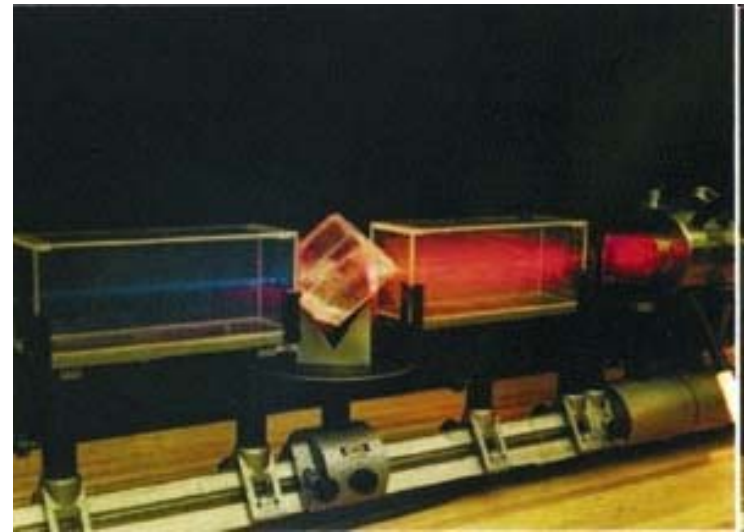
Period doubling crystals

no inversion symmetry

$$P = \chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + \dots$$

$$P_i = \frac{-\partial^2 G}{\partial E_i \partial E_j} E_j + \frac{1}{2} \frac{-\partial^3 G}{\partial E_i \partial E_j \partial E_k} E_j E_k + \dots$$

$$\cos^2(\omega t) = \frac{1}{2}(1 + \cos(2\omega t))$$



806 nm light : lithium iodate (LiIO_3)

860 nm light : potassium niobate (KNbO_3)

980 nm light : KNbO_3

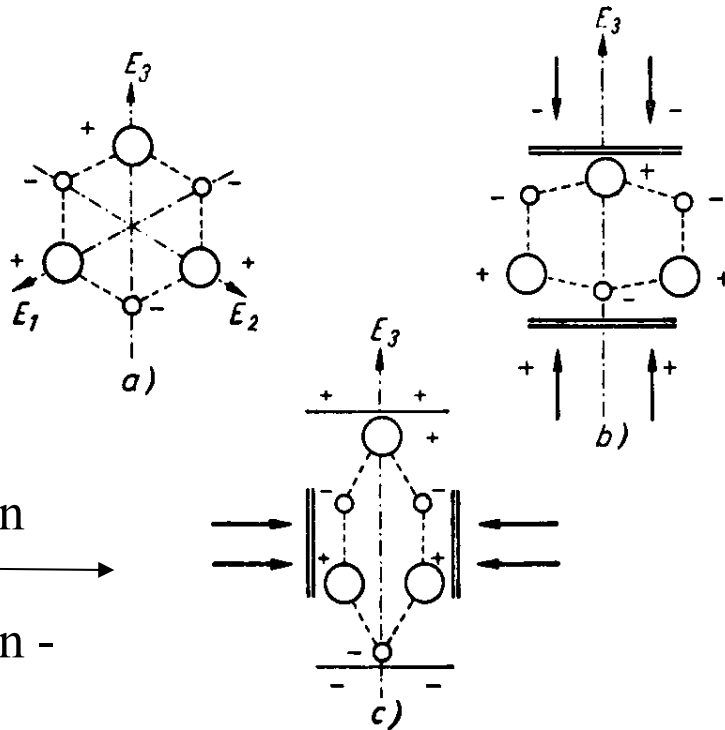
1064 nm light : monopotassium phosphate (KH_2PO_4 , KDP), lithium triborate (LBO).

1300 nm light : gallium selenide (GaSe)

1319 nm light : KNbO_3 , BBO, KDP, lithium niobate (LiNbO_3), LiIO_3

Piezoelectricity

average position
+ is
average position -



$$P_k = - \left(\frac{\partial G}{\partial E_k} \right)$$

average position
+ not
average position -

$$\frac{\partial P_k}{\partial \sigma_{ij}} = - \left(\frac{\partial^2 G}{\partial E_k \partial \sigma_{ij}} \right) = d_{ijk}$$

Rank 4 Tensors

Stiffness tensor

Compliance tensor

Piezoconductivity

Electrostriction

Magnetostriction

How the Seebeck effect depends on stress

How the electric susceptibility depends on stress

How the magnetic susceptibility depends on stress

Nonlinear electric susceptibility

Nonlinear magnetic susceptibility

Electrostriction

$$\frac{\partial P_k}{\partial \sigma_{ij}} = \frac{\partial \epsilon_{ij}}{\partial E_k} - \left(\frac{\partial^2 G}{\partial E_k \partial \sigma_{ij}} \right) = d_{ijk}$$

$$\epsilon_{ij} = d_{ijk} E_k + Q_{ijkl} E_k E_l + \dots$$

piezoelectricity



Electrostriction



Rutile

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From Wikipedia, the free encyclopedia
_symmetry_equiv_pos_as_xyz
1 '-y+1/2, x+1/2, -z+1/2'
Rt 2 'y+1/2, -x+1/2, -z+1/2'
Rt 3 'y, x, -z'
4 '-y, -x, -z'
5 'y+1/2, -x+1/2, z+1/2'
6 '-y+1/2, x+1/2, z+1/2'
Rt 7 '-y, -x, z'
8 'y, x, z'
pa 9 'x+1/2, -y+1/2, -z+1/2'
op 10 '-x+1/2, y+1/2, -z+1/2'
Na 11 'x, y, -z'
th 12 '-x, -y, -z'
13 '-x+1/2, y+1/2, z+1/2'
14 'x+1/2, -y+1/2, z+1/2'
15 '-x, -y, z'
16 'x, y, z'
loop_
_atom_type_symbol
_atom_type_oxidation_number
Ti4+ 4
O2- -2
loop_
_atom_site_label
_atom_site_type_symbol
O _atom_site_symmetry_multiplicity
_atom_site_Wyckoff_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
_atom_site_B_iso_or_equiv
_atom_site_occupancy
_atom_site_attached_hydrogens
Ti1 Ti4+ 2 a 0 0 0 . 1. 0
O1 O2- 4 f 0.30479(10) 0.30479(10) 0 . 1. 0

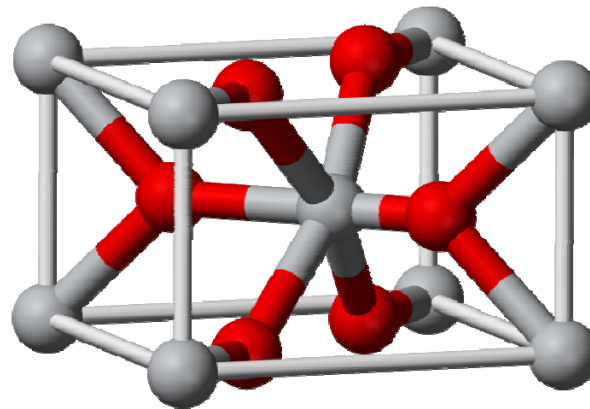
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re known:

al mineral of pseudo-octahedral habit

own crystal, and also exhibits a
it is useful for the manufacture of certain
avelengths up to about 4.5µm.

d **tantalum**. Rutile derives its name from
mens when viewed by transmitted light.



1 high-temperature and high-pressure
s.

able polymorph of TiO₂ at all
energy than metastable phases of
e transformation of the metastable TiO

Rutile



Wine-red rutile crystals from Binn Valley in
Switzerland (Size: 2.0 x 1.6 x 0.8 cm)

General

Category	Oxide minerals
Formula (repeating unit)	TiO ₂
Strunz classification	04.DB.05
Crystal symmetry	Tetragonal ditetragonal dipyramidal H-M symbol: (4/m 2/m 2/m) Space group: P 4/mnm
Unit cell	a = 4.5937 Å, c = 2.9587 Å; Z = 2

Identification

Symmetric and asymmetric tensors

$$-\left(\frac{\partial^2 G}{\partial E_j \partial E_k}\right) = \frac{\partial P_k}{\partial E_j} = \chi_{kj} = -\left(\frac{\partial^2 G}{\partial E_k \partial E_j}\right) = \frac{\partial P_j}{\partial E_k} = \chi_{jk}$$

Symmetric

electric susceptibility
magnetic susceptibility
electrical conductivity
thermal conductivity
stiffness tensor

Asymmetric

Seebeck effect
Peltier effect
piezoconductivity