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Colored gemstones

Any mineral, colored or transparent, may be cut into a gemstones, but only minerals with a Mohs hardness above 6 are wearable and considered gemstones.

The most popular colored gemstones are:

Diamond
Corundum
Beryl
Quartz
Spinel
Topaz
Zircon
Olivine
Epidote
Tourmaline
Garnet
Alexandrite
Kunzite
Feldspar
Turquoise
Lapis Lazuli
Opal

Corundum

Chemistry: Al_2O_3

Crystallography: hexagonal

Physical properties:

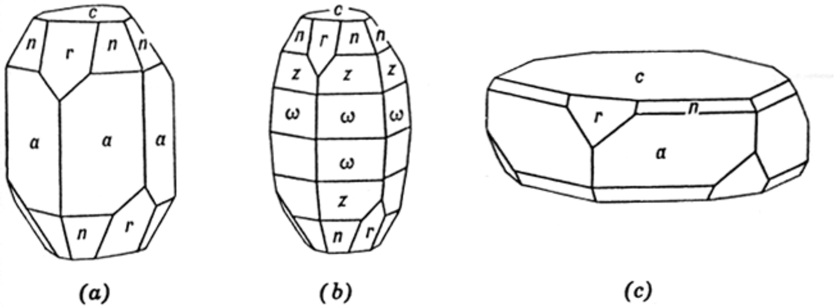
H = 9 D = 4.02 gcm^{-3}
colorless or colored

Occurrence: accessory in metamorphic rocks
detrital mineral in sands

Use: abrasive : emery
gemstone

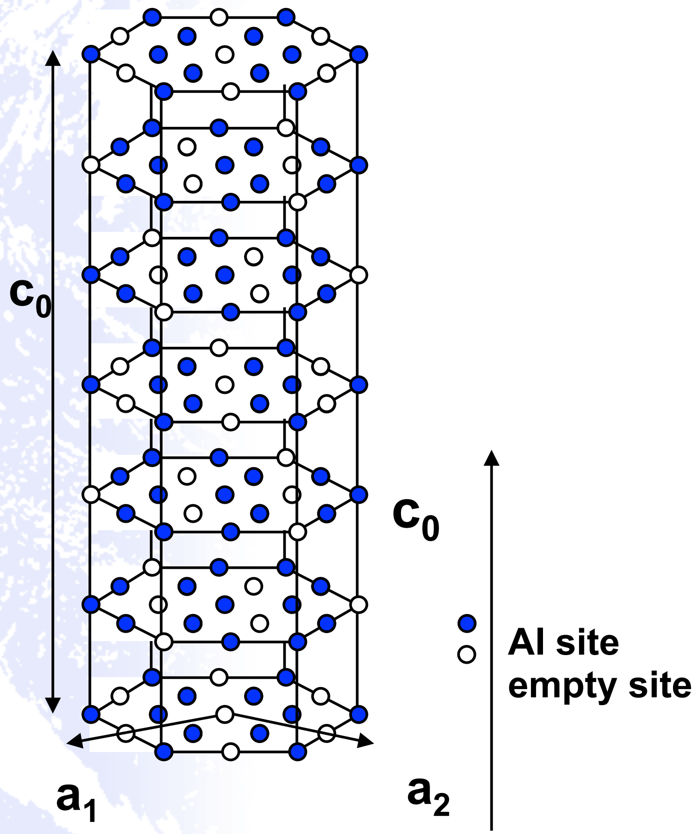
Artificial production

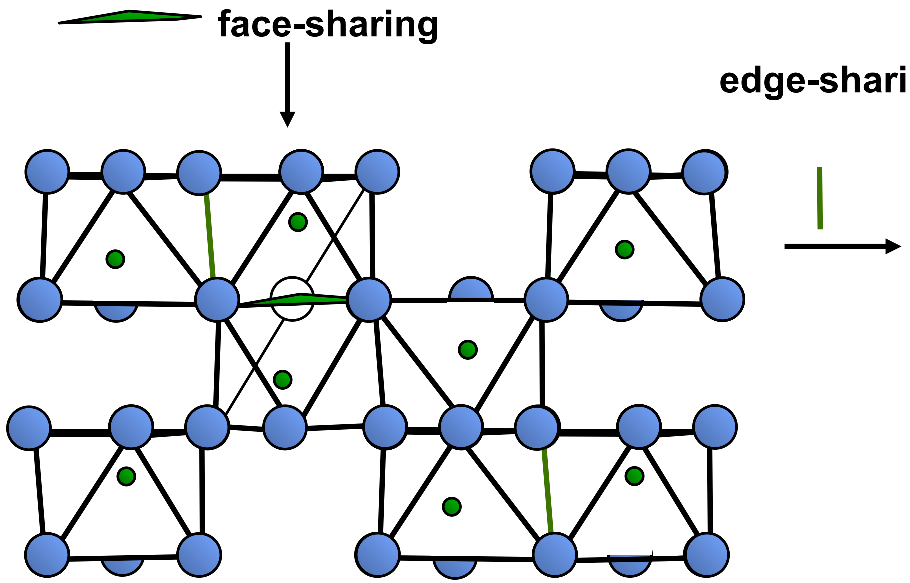
Bright red ruby corundum crystals in white marble matrix.Jagdalak Ruby Mine, Afghanistan. Scale: 4x3.5x3 cm.



Corundum crystal shapes

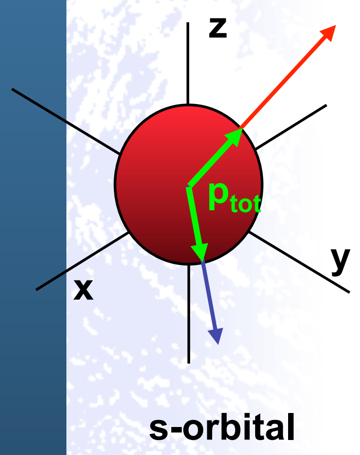
Structure of alpha-Al_2O_3

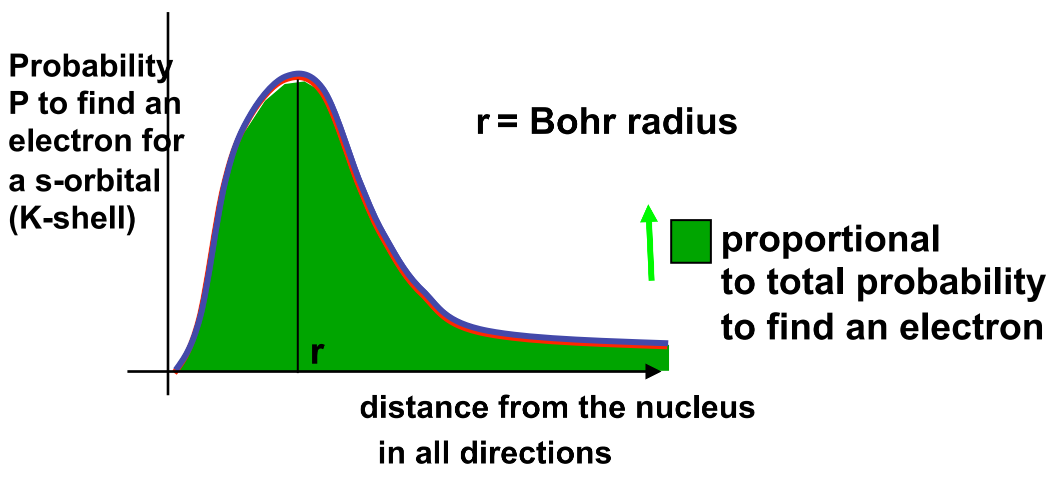


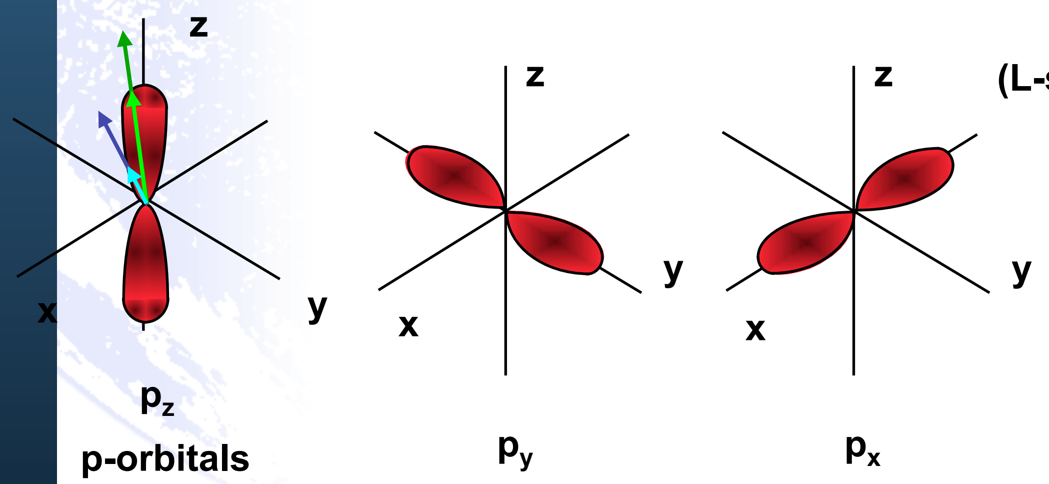


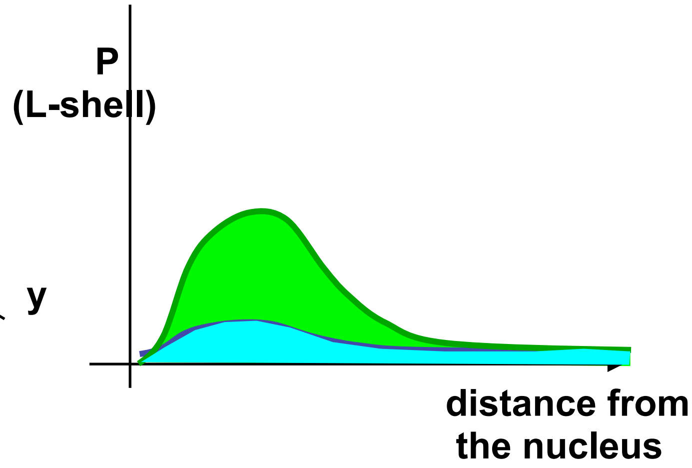
(210) projection of the corundum structure. Aluminum ions in adjacent face-sharing octahedra mutually repell each other.

Schrödinger's atom model







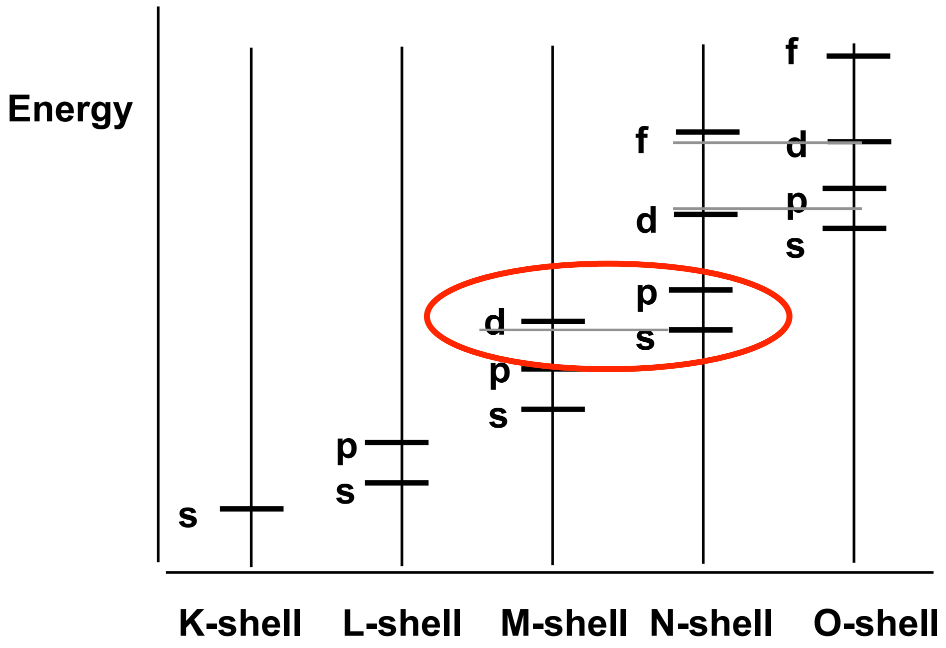


Filling of orbitals

„Relationship“ between Bohr shells and Schrödinger orbitals: Each shell is decomposed into orbitals
K-shell: s-orbital
L-shell: s-orbital, 3 p-orbitals
M-shell: s-orbital, 3 p-orbitals, 5 d-orbitals etc.

Filling of shell’s

General rules:
-Electrons are filled into orbitals in increasing order of their energy levels
-An orbital can have maximum two electrons with opposite spin.
-Every orbital of a subshell has to be filled at least with one electron before they can be occupied by pairs (Hund’s rule).

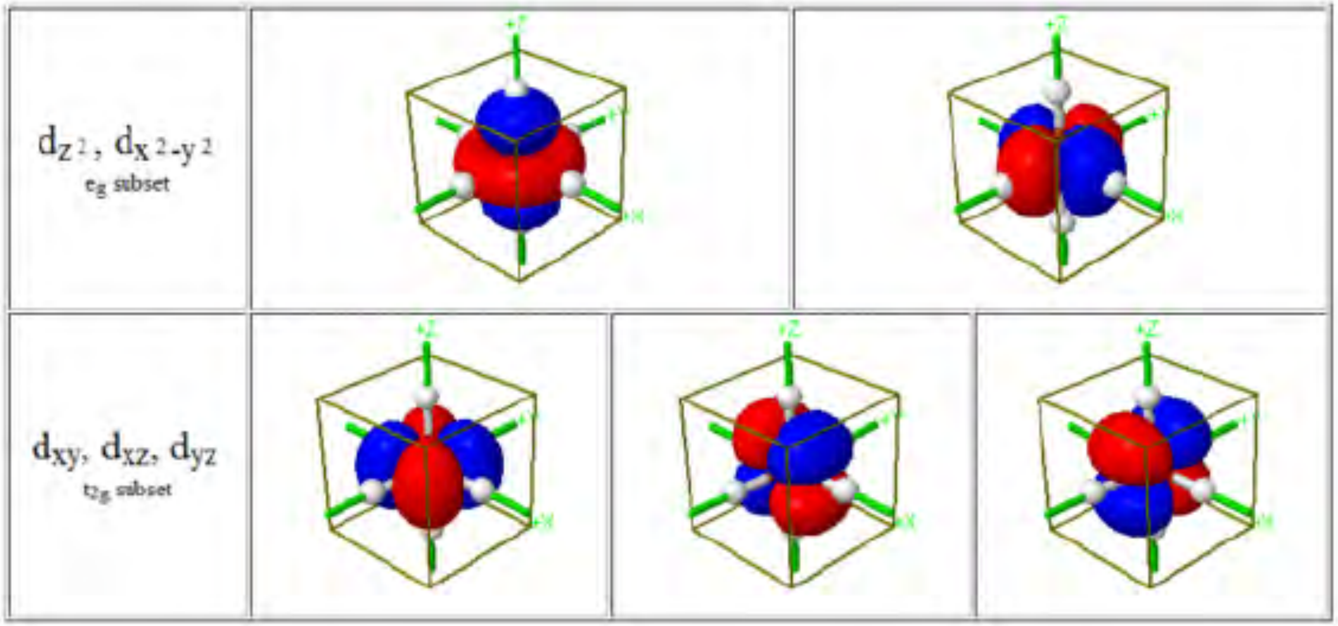


Many exceptions to the rules!

Color due to crystal field splitting I

Occurs in phases containing elements with partially filled d-orbitals

d-orbitals: 5 different geometries possible



In a free atom or ion, electrons in all 5 d-orbital types have the same energyWithin a crystal, however, the relative energies of the orbitals are controlled by the orientation of the orbital lobes relative to the position of the coordinating anions. If the lobes point straight to a anion e.g. to a corner of the coordination polyhedron, the energy will be increased due to the strong repulsive forces between the electrons.

http://www.minsocam.org/MSA/collectors_corner/arc/color.htm

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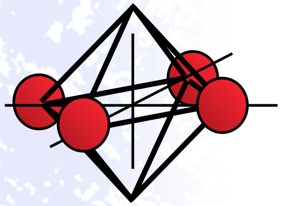
Color due to crystal field splitting II

Example: octahedral coordination

d_{yz}

d_{yz} - orbital lobes point to the faces of the octahedron, e.g. not directly to the coordinating anions. This is true for all other orbitals of the t_{2g} -group.

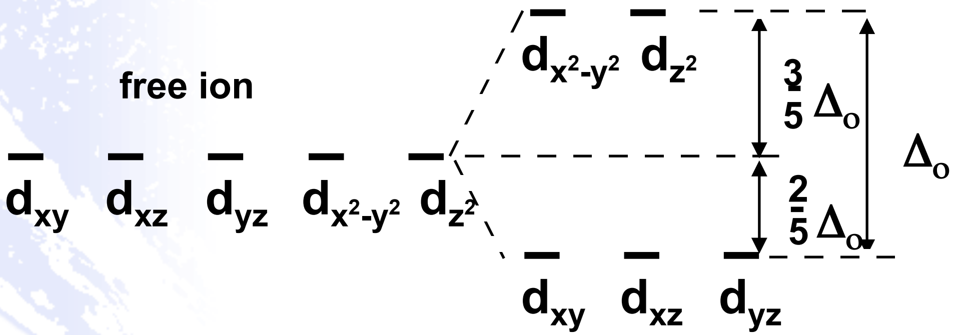


$d_{x^2-y^2}$

$d_{x^2-y^2}$ - orbital lobes point straight to the corners of the octahedron, and, therefore, to the coordinating anions, as do the other e_g -group orbitals.

The energy of an electron in a t_{2g} -group orbital of an octahedrally coordinated atom is, therefore, not only lower than the energy of an electron in a e_g -group orbital, but also lower than the energy of an electron in a free atom.

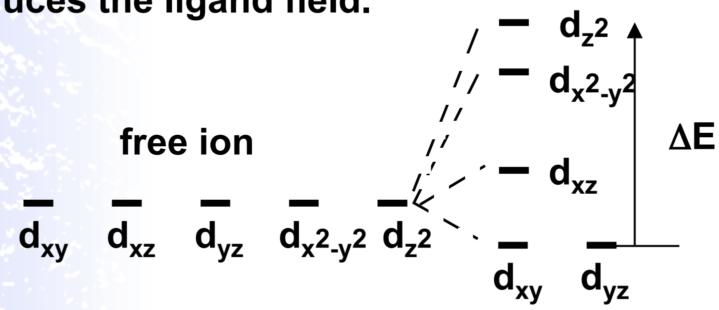
lobes pointing to the corners = high energy



lobes pointing to the faces = low energy

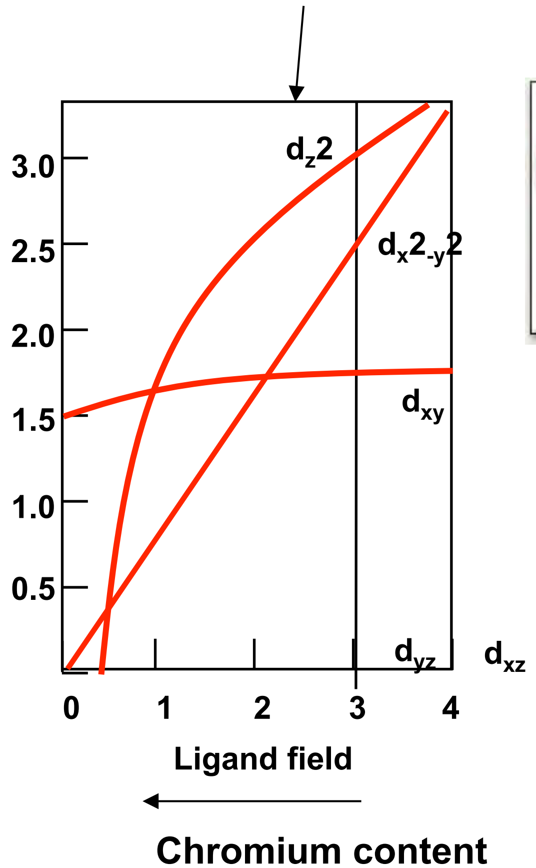
Color of ruby I

Ruby: ppm of Cr^{3+} replacing Al^{3+} in corundum
Complete substitution possible towards Cr_3O_3 (eskolaite)
Octahedra in corundum are not ideal, but slithly distorted. The local distortion increase when the aluminum atom is substituted by f.ex. chromium. The change in the ligand field due to the distortion induces an additional splitting of d-orbital energy levels. The amount of splitting depends on the chromium content.. Higher chromium contents reduces the ligand field.



ΔE

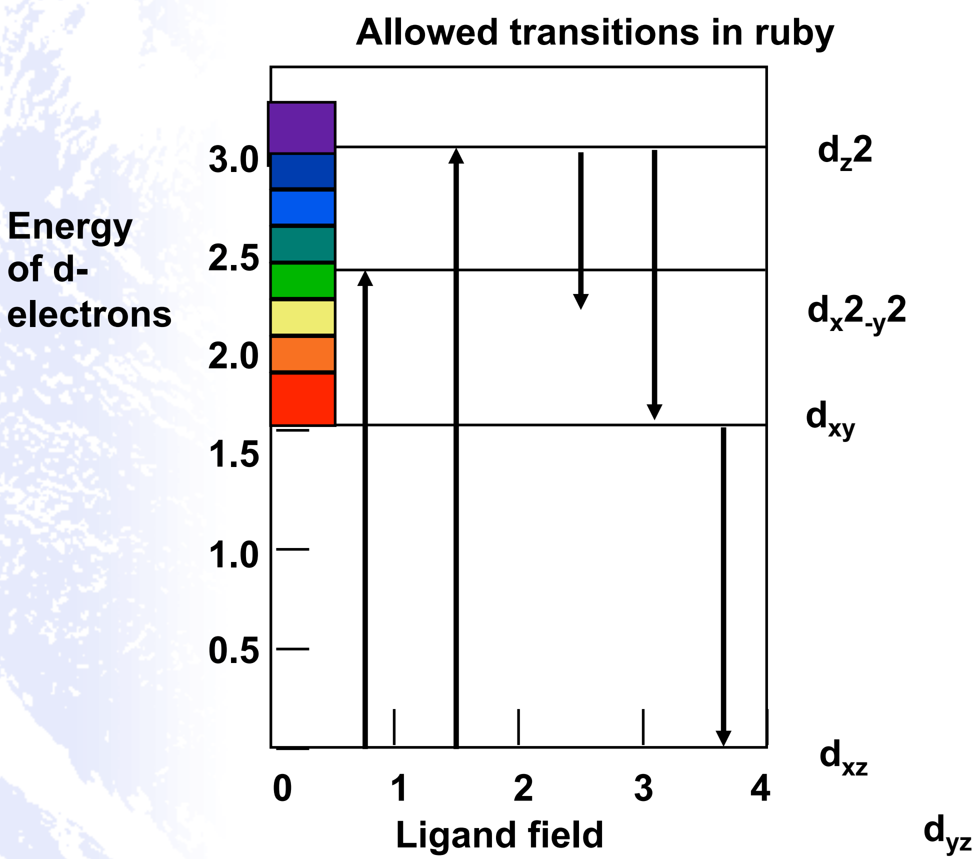
Ligand field in ruby with



The energy differences between the different levels are within the energies typical for wavelengths typical of the electro-magnetic spectrum. Photons can, therefore, excite an electron of the d_{xy} or the d_{yz} into a higher level. The level shown are the zero phonon levels. At finite temperature all levels are broadened by additional phonon energy.

Energy differences between the d_{xy}-d_{yz} and the other orbitals as function of the ligand field strength, which decreases with inreasing chromium content

Color of ruby II



The blue and green parts of the spectrum of visible light are absorbed by excitement of d-electrons into the e_g orbitals. The deexcitation to the d_{xy} level is quick and releases infrared radiation. The deexcitation down to the ground level is slow = red fluorescence.

Color due to electron transfer: sapphire blue

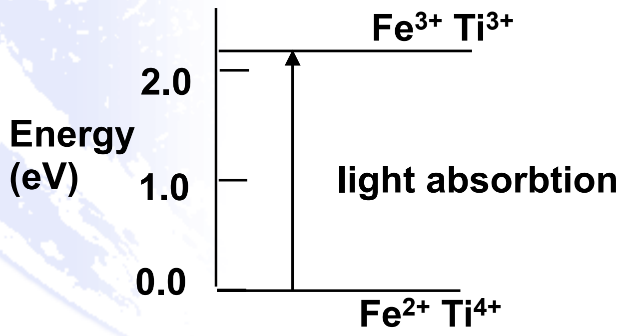
Two types of electron transfer can be responsible for coloring:

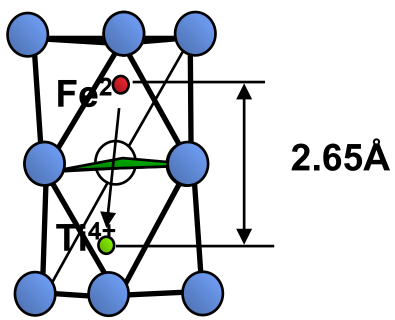
1. Transfer of an electron from an anion to a cation

Example: Transfer of an electron from the filled p - orbital of oxygen into the partially occupied d - orbital of Fe^{3+}. This transition occurs in the ultra-violet with high probability.

2. Electron transfer from one cation into a higher energy orbital of a neighboring cation. Both cations must have different oxidation state, and are in neighboring edge or face sharing coordination polyhedra. The distance between the cation is usually small.

Example: Corundum with trace amounts of Fe^{2+} and Ti^{4+}.
Transfer of an electron from Fe^{2+} to Ti^{4+}:





The energy adsorbed by the electron transfer corresponds to the red part of the spectrum, the complementary color is thus blue green, the color of sapphire.

Ruby

Red gem quality corundum

Color dew to a few ppm of Cr

Famous places : Burma (Mogok)
Kenya, Ceylan, Thailand

Sapphire

Blue colored gem corundum
(may also be used for other color varieties)

Color due to small amounts of Fe and Ti

Famous places : Cambodia, Kashmir, Australia

Colors of gem quality corundum

Corundum mining

Important gem corundum mining districts of the world

Price of rubies and sapphire

With the exception of imperial jadeite and certain rare colors of diamond, ruby is the world's most expensive gem. But like all gem materials, low-quality (i.e., non-gem quality) pieces may be available for a few dollars per carat. Such stones are generally not clean enough to facet. The highest price per carat ever paid for a ruby was set on April 12, 2005 for an 8.01-ct. faceted stone that sold for $274,656 per carat ($2.2 million) at Christie's New York (right). Previously the record for per-carat price was Alan Caplan's Ruby ('Mogok Ruby'), a 15.97-ct. faceted stone that sold at Sotheby's New York, Oct., 1988 for $3,630,000 ($227,301/ct).

Origin and price I

Colored stones are graded against the same 4 C's as diamond, but an additional factor influencing the price is the origin of the stones. The latter has to be included into the certificate.

Table B.1: Ruby (including pink) prices – cut stones

Origin	Size (ct)	Quality & price per carat (in US$; K=1000)				
		Poor	Fair	Good	Very Good	Exceptional
Burma, Mogok (certified, untreated)	< 0.49	1–25	25–50	50–300	300–600	-
	0.5–0.99	1–60	60–350	350–700	700–3K	3K–4K
	1.0–1.99	1–400	400–800	800–3.5K	3.5K–4.6K	4.6K–10K
	2.0–4.99	1–900	900–1.5K	4K–5.3K	5.3K–11.5K	11.5K–125K
	5.0 +	1–1.2K	1.5K–6.1K	6.1K–13.2K	13.2K–144K	144K–225K
All other sources* Afghanistan, Jagdalek Burma, Mogok, Mong Hsu Kenya Sri Lanka Tanzania Thailand / Cambodia Vietnam (all generally heat treated)	< 0.49	1–25	25–50	50–300	300–500	-
	0.5–0.99	1–60	60–350	350–575	575–2.3K	2300–3.5K
	1.0–1.99	1–400	400–650	650–2.6K	2600–4K	4K–6K
	2.0–4.99	1–700	7.5K–3K	3K–4.6K	4.6K–7K	7K–20K
	5.0 +	1–1K	1K–5.3K	5.3K–8K	8K–23K	23K–100K

Origin and price II

Table B.2: Blue sapphire prices – cut stones

Origin	Size (ct)	Quality & price per carat (in US$; K=1000)				
		Poor	Fair	Good	Very Good	Exceptional
Kashmir, India	1.0–1.99	1–300	300–2K	2K–3.4K	3.4K–4.5K	4.5K–7.55K
Mogok, Burma	2.0–3.0	1–500	500–3.9K	3.9K–5.2K	5.2K–8.7K	8.7K–11K
(certified, untreated)	3.0–4.99	1–700	700–6K	6K–10K	10K–12.7K	12.7K–13.5K
	5.0 +	1–1K	1K–11.5K	11.5K–14.6K	14.6K–15.5K	15.5K–45K
All other sources	< 0.49	1–35	35–175	175–200	200–300	-
Australia	0.5–0.99	1–200	200–225	225–350	350–500	700–1.5K
China	1.0–1.99	1–250	250–450	400–575	575–700	1.7K–3K
Montana, USA	2.0–4.99	1–500	500–850	650–800	800–1.7K	3.5K–10K
Nigeria	5.0 +	1–975	975–1.1K	1.1K–2K	2K–3.5K	
Sri Lanka						
Tanzania						
Thailand / Cambodia						
Vietnam						
(all generally heat treated)						

Origin and price II

Prices for Mogok rubies:

(1.00 - 1.49 CT) 1.35 to 1.49 Ct may trade at 20% to 25% premiums over 1 Ct.

	Pigeon Blood	Golden Red	Bright Red	Pinkish Red	Pastel Red	
IF	5,800	3,700	2,700	1,800	1,400	IF
VVS	3,200	2,200	1,600	1,000	800	VVS
VS	1,950	1,300	900	450	400	VS
SI	1,500	1,000	600	300	270	SI
I	750	400	300	225	125	I

All Unheated RUBY may trade at significant premiums to the price list in speculative market.

(5.00 - 5.99 CT)

	Pigeon Blood	Golden Red	Bright Red	Pinkish Red	Pastel Red	
IF	93,000	81,000	58,500	39,000	27,000	IF
VVS	54,000	45,000	30,000	15,000	12,000	VVS
VS	27,000	16,500	11,500	6,000	5,500	VS
SI	18,000	11,000	6,600	4,800	3,900	SI
I	12,000	8,000	4,500	3,000	2,550	I

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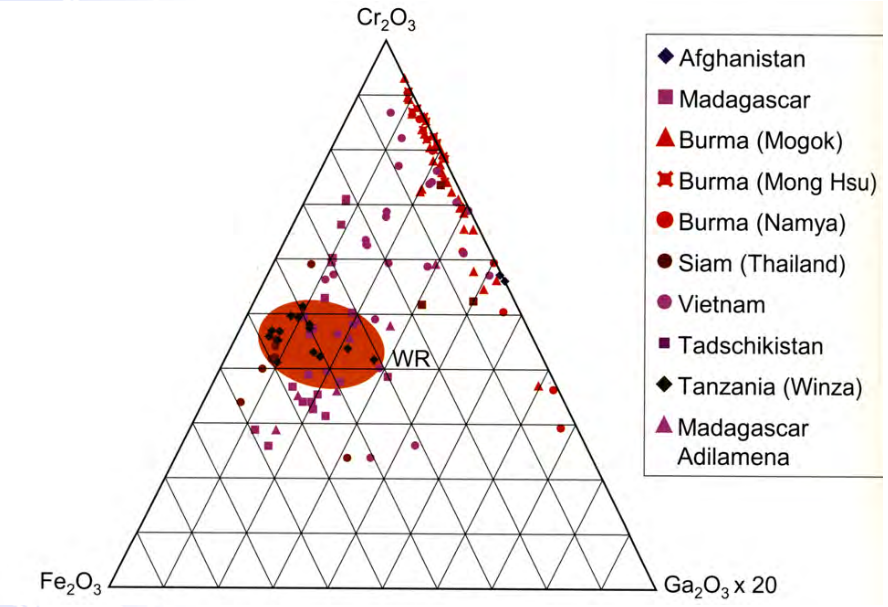
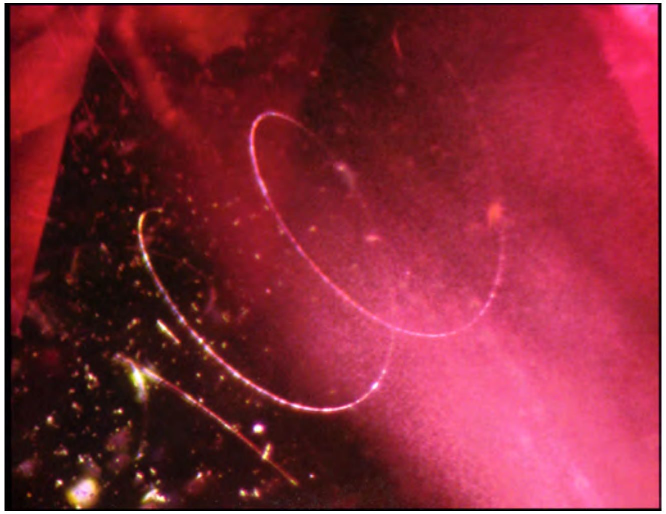
Origin of rubies

Origins of rubies and colored stones in general may be determined using chemical (trace elements inclusions) and physical (optical properties) as fingerprints. In the last year rubies from Tansania appeared on the market. Inclusions and chemical fingerprints allow to discriminate these rubies from Winza against other locations.



Ternary chromium -iron - gallium oxide diagram. The Winza rubies can be discriminated against the Burma rubies which have similar appearance



Typical helical inclusion/defect trail in a Winza ruby. The nature of this feature is unknown.

Ruby certificate

GRS GEMRESEARCH SWISSLAB®

No	eGRS2001-Sample
Date	8th December 2001
Object	One faceted gemstone
Identification	**Natural Ruby**

Origin

Gemmological testing revealed characteristics corresponding to those of a natural ruby from:

Burma (Mogok, Myanmar)

Weight	6.03 ct
Dimension	10.78 x 9.99 x 5.87 (mm)
Cut	brilliant/step
Shape	cushion
Color	vivid red (GRS type "pigeon's blood")
Comment	No indication of thermal treatment

Dr. A. Peretti FGG FGA

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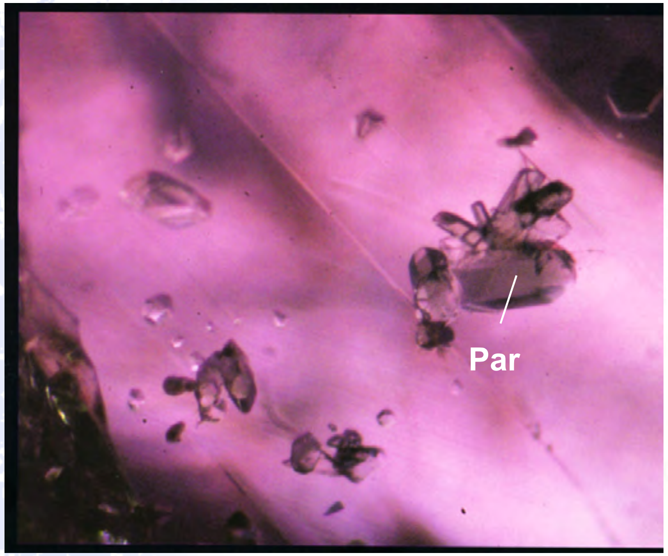
Pargasite inclusions in Winza rubies



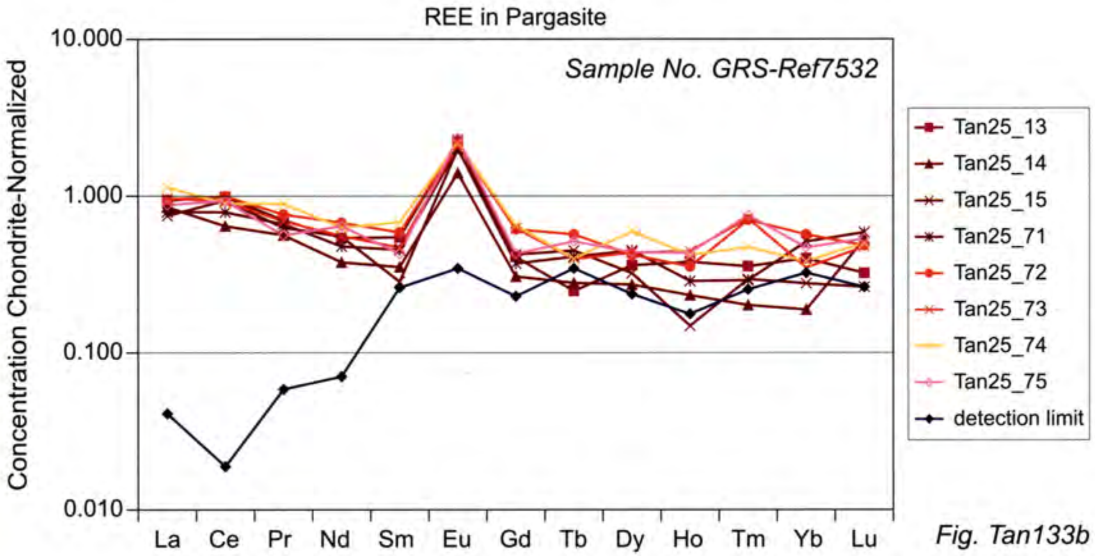


Fig. Tan133b

Pargasite inclusions, with typical positive europium anomalies are an additional fingerprint, which, together with the other fingerprints, allow to discriminate Winza rubies from the other known ruby locations.

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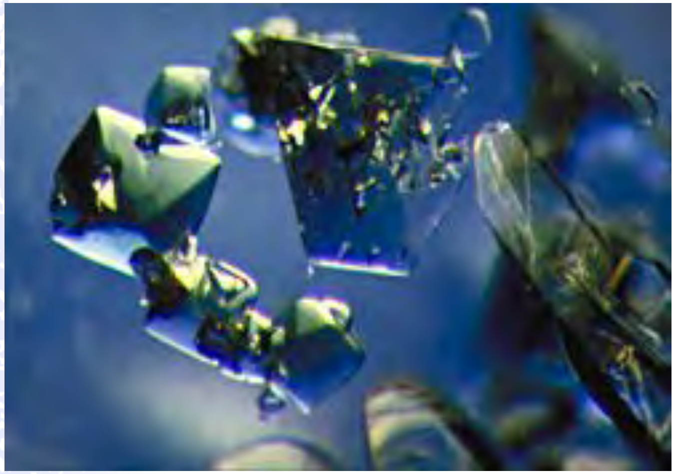
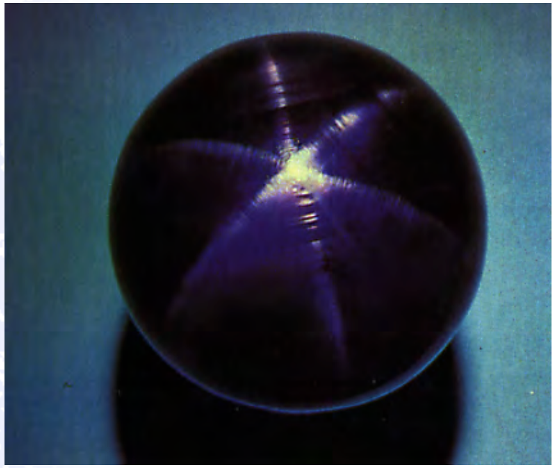
Apatite and spinel inclusions



Spinel octahedra in a blue sapphire from Sri Lanka; 25x.

Light yellow apatite crystals in a corundum from Umba Valley, Tanzania; 25x.

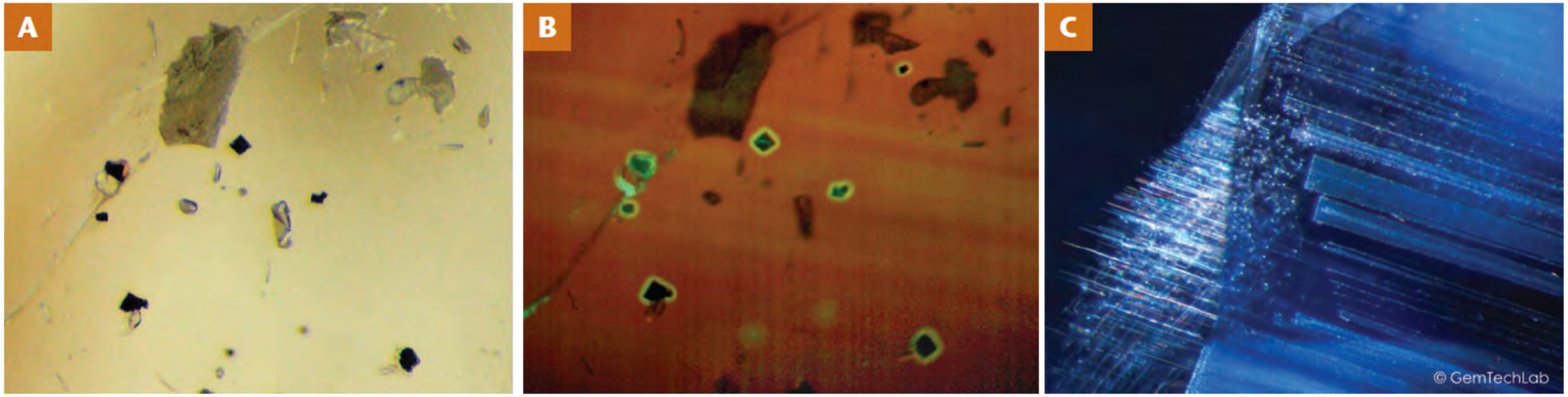
Legendary sapphires



Star of asia, a star sapphire spere of 330 carats. It belonged to the Maharadja of Jodpur. The six branched star is due to inclusions of rutile needles. The diffraction effect due the needles is called asterims.

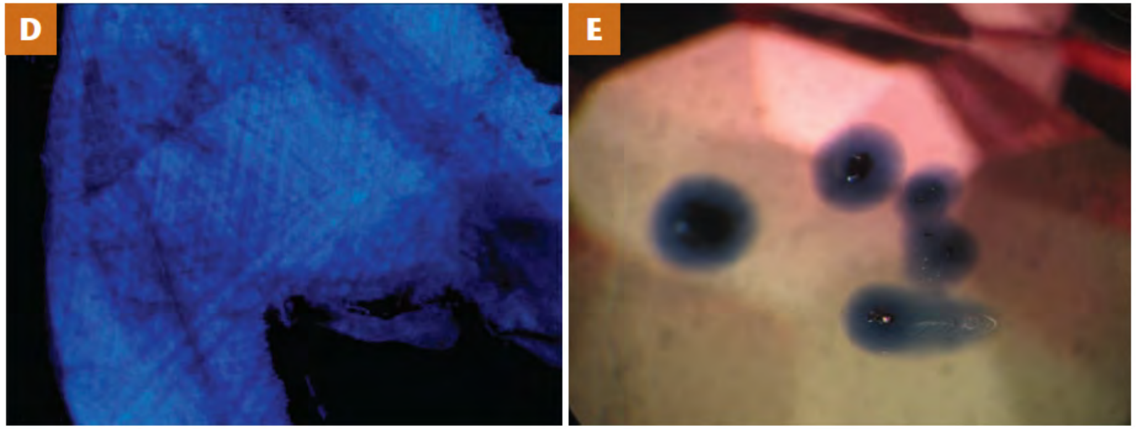
Logan sapphire, 330 carats. Natural History Smithsonian Institution, Washington DC.

Inclusions in Mogok sapphires



Natural Inclusions in sapphire (A, B) Micrographs of a yellow, unheated sapphire from Mogok, Myanmar, with fluid, calcite, and U-rich thorianite [(Th,U)O2] inclusions. Field of view ca. 1.8 mm. Transmitted light, in B additional UV light, reddish luminescent background due to traces of Cr3+, a yellow luminescent zoning due to color centers associated with traces of Mg2+ (invisible in transmitted light), and bright yellowish green luminescent halos around the U-rich thorianite crystals. (C) Rutile needles ("silks," on the left) and polycrystalline böhmite (on the right). The aspect of these inclusions in this 12.69-carat blue sapphire from Myanmar proves that the stone has not been subjected to HT treatment.

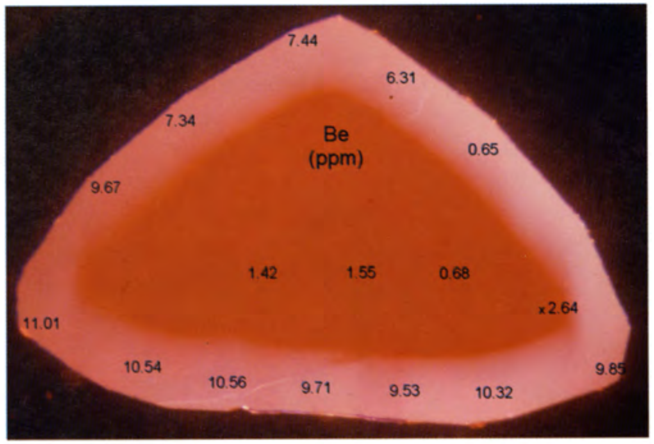
Treated Mogok sapphires



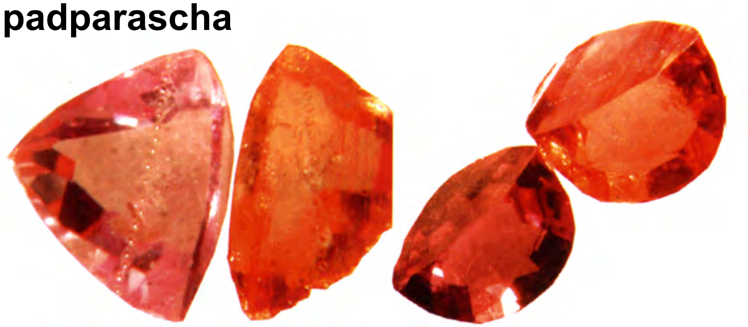
(D) Heat treatment in sapphire causes the diffusion of Ti from rutile inclusions into the corundum, enhancing its blue color and leaving in some cases "ghosts" of rutile silks, as in this treated 6.46-carat sapphire. (E) This image is typical of Be-diffusion treatment applied to a sapphire from Songea (Tanzania); yellowish and orangey zones of color were induced by the treatment. The observation of blue diffusion halos ("frog eggs") around the stubby rutile inclusions typical of Songea is indicative of both heat treatment and the geographic origin. This exemplies how, in some cases, classical gemology can detect Be-diffusion treatment, which otherwise requires microdestructive LA–ICP–MS or LIBS analysis of Be when it leaves no typical traces. Field of view ca. 2 mm. micrograPhs A,B,C,D: F. Notari; E: E. Fritsch

Diffusion treatment of natural rubies and sapphires

In addition to heat treatments already discussed for diamonds, natural colored stones are modified by incorporating color giving elements by diffusion treatment. Diffusion treated stones are depreciated relative to untreated stones of same quality. It is, therefore, crucial to be able to identify diffusion treatments. A famous example is a novel diffusion treatment with beryllium of yellow and red corundum which turned them orange. This color tone, called padparadscha, is rare in nature. Large numbers of such treated padparadschas appeared at the beginning of the century on the market, all knew that they were treated but nobody was able to prove it. Only sopphisticated laser ablation ICP-MS and SIMS work allowed to identify the small amount of beryllium in these stones.

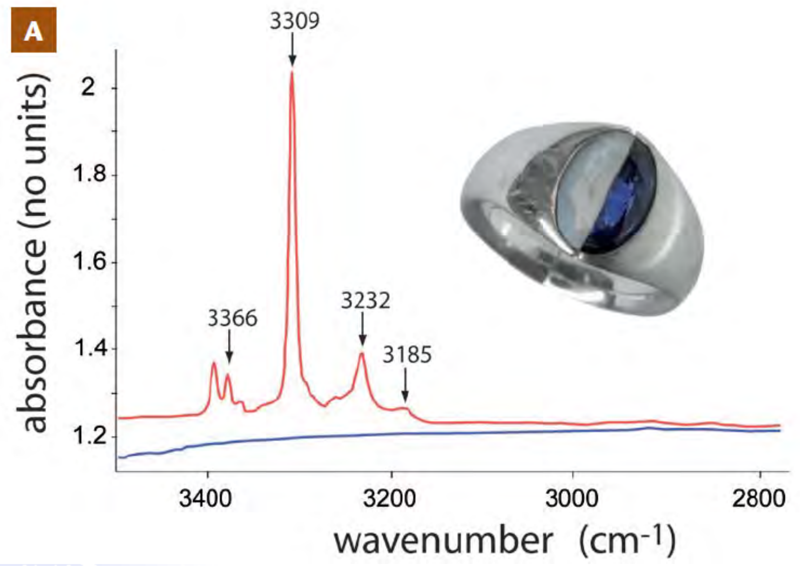


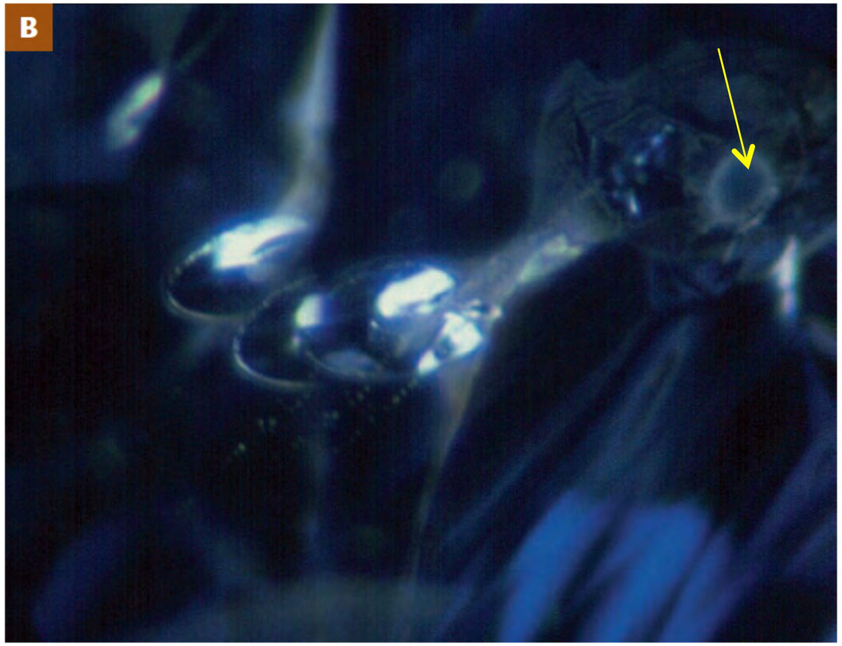
Laser ablation ICP-MS measured Be concentration in a diffusion treated padparascha



Pink and red-brown rubies before and after Be diffusion treatment

Diffusion treatment of natural milky sapphire





One half of the sapphire in the ring (A, inset) has been heat treated to a desirable transparent blue from an initial valueless milky appearance. High-temperature treatment is revealed by optical microscopy (B); the zircon inclusion in the top-right corner (yellow arrow) has melted and now looks like a whitish sphere ("golf ball" inclusion), and needle-like TiO2 (silk) inclusions in the center have been partially dissolved and now appear as dotted lines. 40x magnication. Transmission infrared spectroscopy (A) provides further information: the peak at 3309 cm-1 and its companions indicate heat treatment under reducing conditions, with capture of an H atom by an Fe–Ti pair (red spectrum), absent in the untreated part (blue spectrum). ring Photo courtesy Pascal Entremont

Tourmalines

Tourmaline group. The crystal show a continuous color change from blue to rose

$(Na,Ca)(Li,Mg,Al)_3(Al,Fe,Mn)_6(BO_3)_3 Si_6O_{18} (OH)_4$

There are 25 accepted endmembers in the tourmaline group and even more „color varieties“. The most important endmembers are:

Schorl	Fe dominant, black
Dravite	Mg dominant, brown
Elbaite	Li dominant, green, rosa

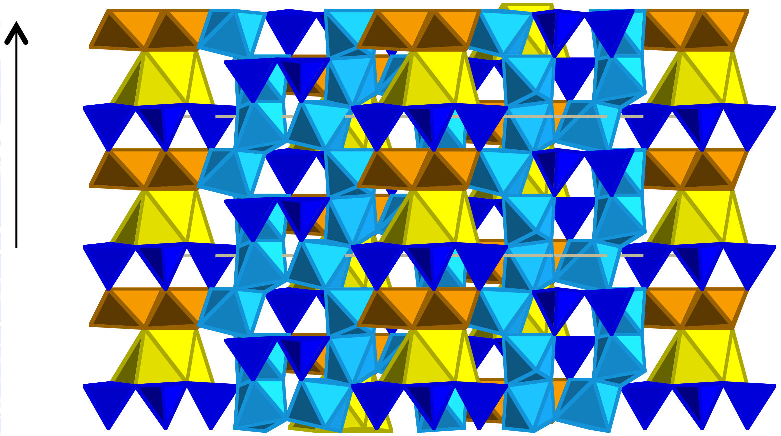
Mohs hardness: 7 - 7.5

Refraction indices: 1.610 - 1.675

Density:3.0 - 3.25

Tourmaline crystal structure

c-axis =
polar axis



Tourmaline structure seen along [100].
dark blue: silicium tetrahedra
light blue: octahedra (Al)
brown: octahedra (Fe, Mg etc.)
yellow: large alkali cations
The triangular coordinated boron atoms are not shown.

Of the thirty-two crystal classes, twenty-one are non. The property of these crystal classses is that for a vector [u,v,w], there is no equivalent directio [-u,-v,-w]. Ten of these represent the polar crystal classes. In this classes any sum of vectors related by symmetry to the polar direction is ≠ 0. This is the case for 3m, the crystal class tourmaline belongs to. The polar axis is the c-axis. The threefold axis and the mirror parallel to it produce vectors which point all into the same direction e.g. the sum of such vectors is always ≠0. The gradual color change observed in some tourmalines is due to this permanent polarization. Some color giving elements prefer the positive, others the negative pole.º

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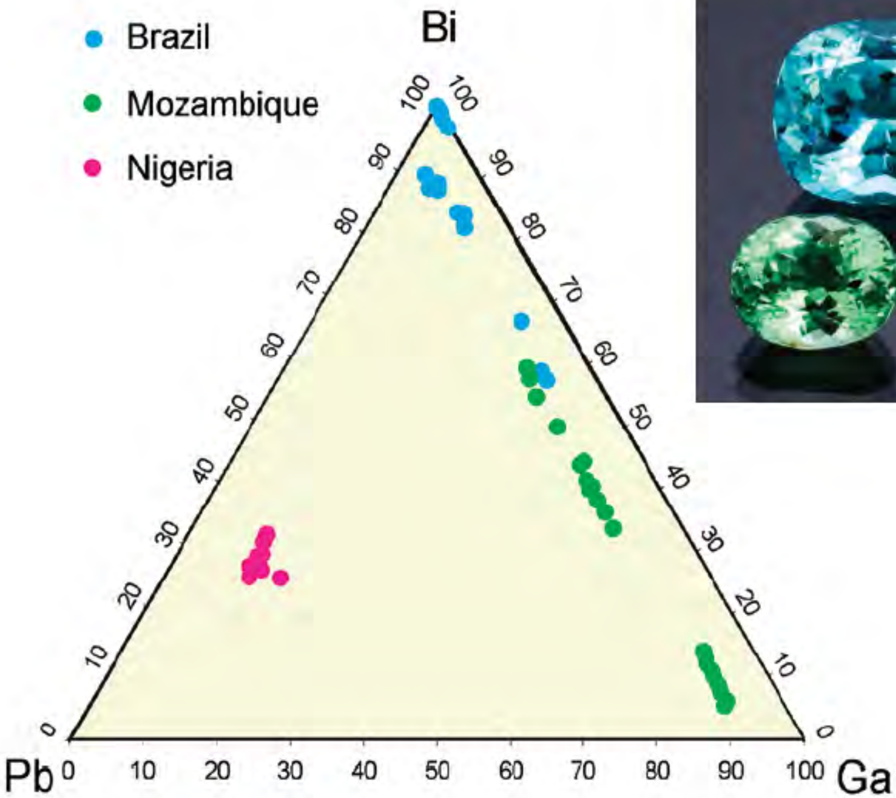
Color in tourmalines

Cut tourmalines close to the elbaite endmember $Na(Li_{1.5}A_{1.5})Al_6(BO_3)_3Si_6O_{18}(OH)_4$ a species that would be devoid of color if it were exactly the ideal composition. The color are due to crystal field effects (deep blue: Cu^{2+}, light blue: Fe^{2+}, pink: Mn^{3+}) and charge tranfer (green: Fe^{2+}-Ti^{4+})

Origin of Paraiba type tourmalines

Copper containing tourmalines have beautyful intense mainly green and blue colors. There are three provenances known for such stones: Nigeria, Mozambique and Brasil (Paraiba). Concentration of traces like Bi, Ga and Pb allow to discriminate between the origins. Such analyses, however only possible with sophisticated techniques i.e. La-ICP-MS or LIPS.



Bernard Grobéty 2012

Beryl

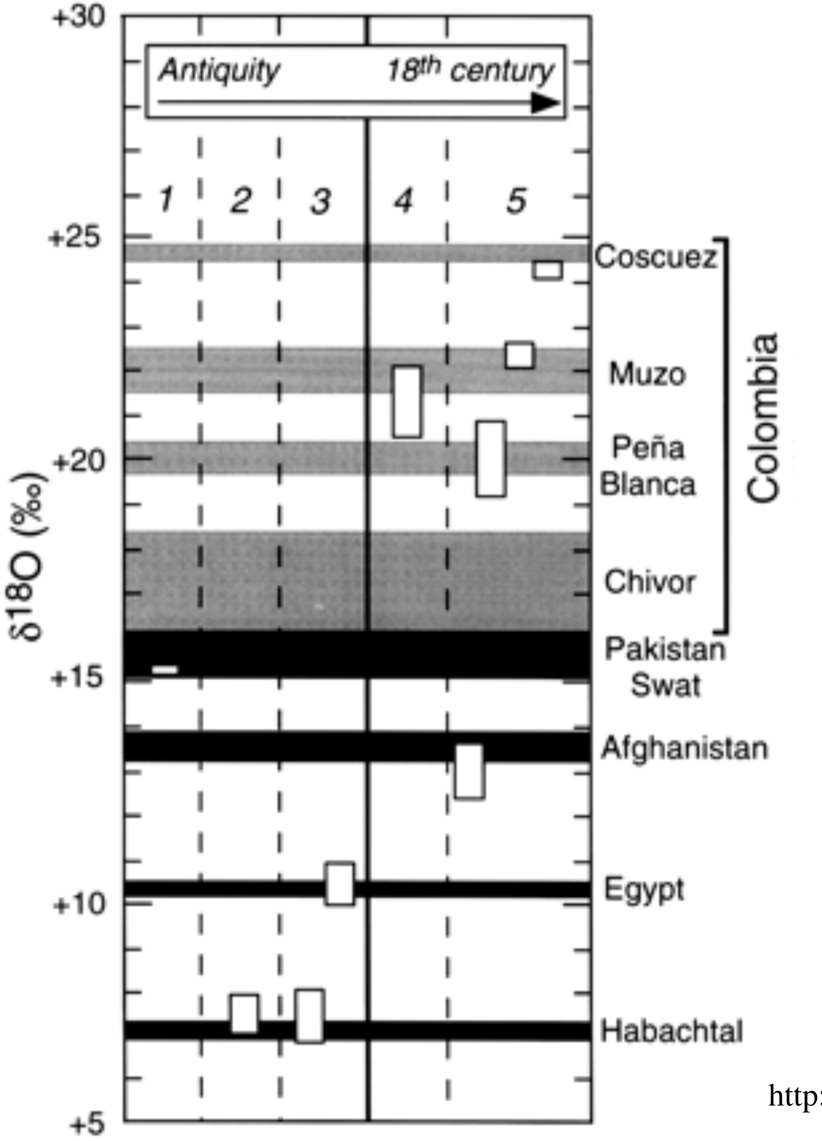
$Be_3 Al_2 (Si_6O_{18})$
Mohs hardness:7.5 -8
Refractive indices n: 1.58 - 1.60
Densité: 2.63 - 2.8

Color varieties of beryl:

green	emeralds	CF Cr^{3+}
blue	aquamarine	CF Fe^{2+}
golden	heliodor	CF Fe^{3+}
rose	morganite	CF Mn^{2+}

CF: crystal field effect

Origin of emeralds: oxygen isotope studies



Beryls from the most important localities differ strongly in their oxygen isotope signature. The latter can, therefore, be used to test the provenance of beryls. This technique has been used to proove the all antique emeralds (Egyptian, Roman finds) are from Asia and Europe, but not from South America. 1: Gallo-Roman earring; 2: Holy Crown of France; 3: Haüy's emeralds; 4: Spanish galleon wreck; 5: "old mine" emeralds. Giuliani et al (2000)

http://www.crpg.cnrs-nancy.fr/Science/Emeraudes/Introduction.html

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Synthetic colored gemstones

Shown here are synthetiux-grown emeralds produced by Gilson (3, 6, 7), Seiko (5), Lennix (8), Inamori (9), and Chatham (10, 11, 12), as well as Russian hydrothermal (1, 2) and Russian (4) synthetic emeralds. The blue synthetic sapphire crystals (13, 15) were grown by Chatham flux environment, and the faceted blue sa-phire (14) by a melt method. The synthetic rubies were made by several methods: Russian hydrothermal (16, 17), Chatham flux (19, 22), Douroux (18, 21), Ramaura flux (20, 23), and Kashan flux (24, 25). The faceted synthetic stones range in weight from 1.21 to 6.57 cts, and the synthetic crystals range from 10.21 to 482.51 cts. Synthetica courtesy of thomas chatham; photo © tino hammid and robert e. Kane

Synthetis methods

TABLE 1 GENERAL CATEGORIES OF GEM AND MINERAL CRYSTAL-GROWTH TECHNIQUES

MELT GROWTH
Solidification in a container
Czochralski growth (pulling from a seed in contact with the corresponding melt)
Verneuil or flame-fusion growth (projecting molten oxides from a flame on a seed)
Zone growth (crystallizing from a seed in a corresponding powder, locally molten)
Skull melting (mass crystallization from a molten volume using the same unmelted powder as the crucible)
SOLUTION GROWTH
Growth from water or other solvents
Gel reaction growth
Hydrothermal growth (growth in a fluid under an appropriate pressure and temperature)
Flux and flux zone growth (growth in an anhydrous molten salt)
Growth by electrolysis
High-pressure flux growth
VAPOR PHASE GROWTH
Sublimation growth
Growth by reaction in a vapor phase
Chemical vapor phase transport growth

ADAPTED FROM NASSAU (1980)

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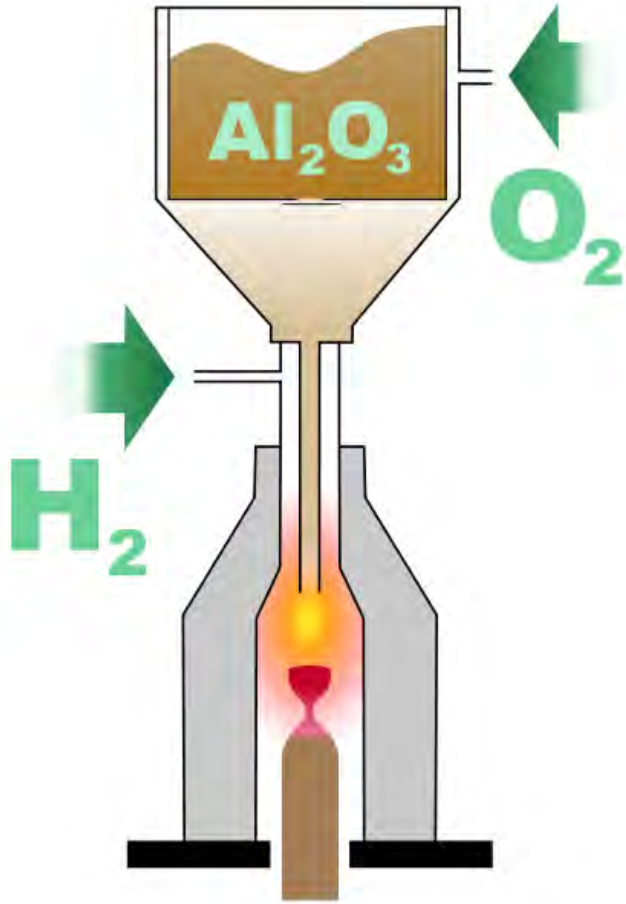
Synthetic rubies and sapphires

Synthetic corundum and color varieties thereof are manufactured by the Verneuil process. Corundum powder with color giving additions are mixed with oxygen and pushed through and nozzle. At the exit of the nozzle hydrogen is added and ignited the corundum melts and the droplets fall on a seed crystal. The distance of the latter is such, that the corundum remains melted at the surface. The seed crystals is then retracted at the same rate melt is added. The retracted part crystallizes to a boullion.
A world leader in the production of synthetic rubies is DJEVA Inc. in Monthey (Valais).



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Treatments of gemstones

Symbol	Definition
A	Indicates either a gemstone that is not currently known to be enhanced or one that is so rarely enhanced that to give it an "E" symbol would mislead the public. Example: Amethyst is rarely known to be treated.
E	Indicates that this gemstone is routinely enhanced.
N	Indicates this particular gemstone has received no enhancement and the seller will guarantee this.
B	Indicates that bleaching of the gemstone has been done. Bleaching is the use of chemicals or other agents to lighten or remove a gemstone's color. Example: 'Blonde Tigereye" this way.
C	Indicates that a Coating has been used as a surface treatments such as waxing, lacquering, enameling, inking, foiling, or sputtering of films to improve appearance, provide color or add special effects.
D	Indicates that dyeing has occured. Dyeing is the introduction of coloring matter into a gemstone to give it new color, intensify present color or improve coloruniformity. Example: Agate is enhanced this way
F	Indicates the gemstone has had filling(cracks and pores) or stabilizing with colored or colorless glass, plastic or other hardened material to improve appearance, durability, and/or weight. Example: Turquoise is commonly enhanced in this manner.
G	Indicates the gemstone has undergone some form of Gamma or Electron Irradiation to alter a gemstone's color. Example: Blue Topaz is commonly enhanced in this manner.
H	Indicates the stone has been heated to effect desired alteration of color, clarity, and/or phenomena. Example: Sapphire and citrine are commonly enhanced in this manner.
L	Indicates the gemstone has undergone the use of a laser and chemicals to reach and alter inclusion.Example: Diamond is sometimes enhanced in this manner.
O	Indicates the introduction of a colorless oil, wax, natural resin, or unhardened man-made materials into fissured or porous gemstones was made to improve appearance. Example: Emerald
R	Indicates the gemstone has undergone Irradiation. This is the use of neutron or a combination of neutron with any other bombardment to alter a gemstone's color. Example: Blue Topaz
U	Indicates the gemstone has undergone Diffusion which is the use of chemicals in conjunction with high temperatures to produce a relatively shallow subsurface layer of color and/or asterism-producing inclusions. Example: Difrusion treated Sapphire is enhanced in this manner.