MINIFORUM CYTED-IBEROEKA

Valorização de Pegmatitos Litiníferos

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Quartz from Granite Pegmatites : a Raw-Material for High-Technology

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The strategic value of natural crystals of quartz – one of the most abundant and pure minerals in the Earth's Crust - was clearly established by the application in sonars during the Second World War, following the development of an ultrasonic submarine detector.

Crystals from Brasil and Arkansas/USA pegmatites were initially used in numerous and diversified technological applications but, by the end of the sixties, these natural crystals were overpassed by synthetic ones – *cultured quartz crystals* – nowadays intensively produced by Japan, United States, Russia and China.

Under strict conditions of purity, the fragments of natural quartz crystals produced when dismantling granite pegmatites – *lascas* or *taliscas* – configure a valuable raw material for the production of crystalline quartz with electronic quality having multiple piezoelectric and optic applications in various "high-tech" artifacts such as sensors, accelerometers, microphones, electronic transducers, etc.

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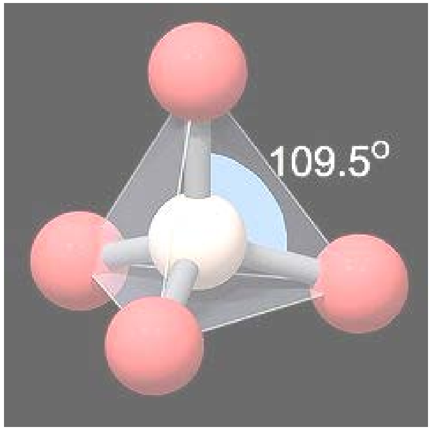
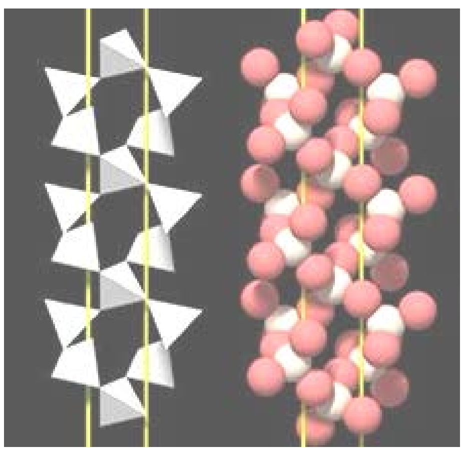
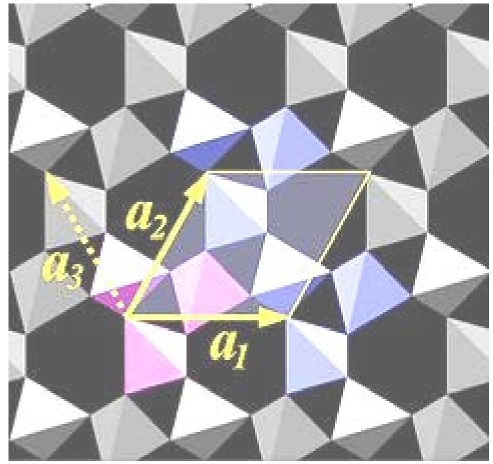
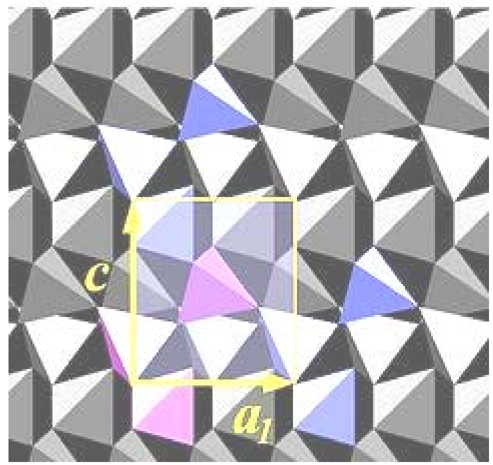
Quartz crystal structure

$[SiO_4]$ tetrahedron

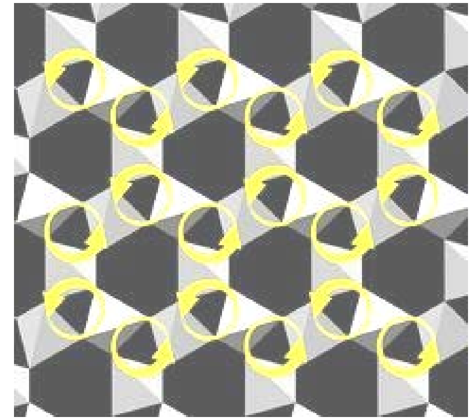


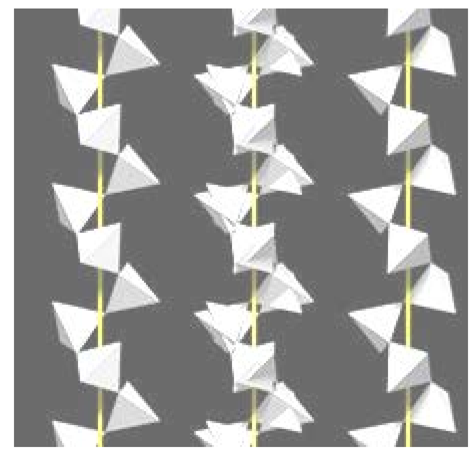






Spirals of tetrahedra





http:/www.quartzpage.de/gen_struct.html

Polarity and optical properties

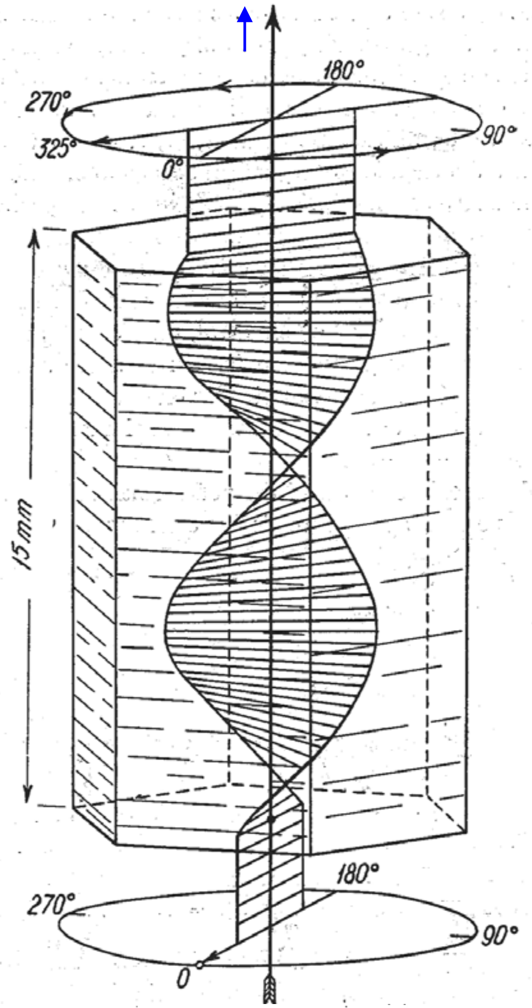
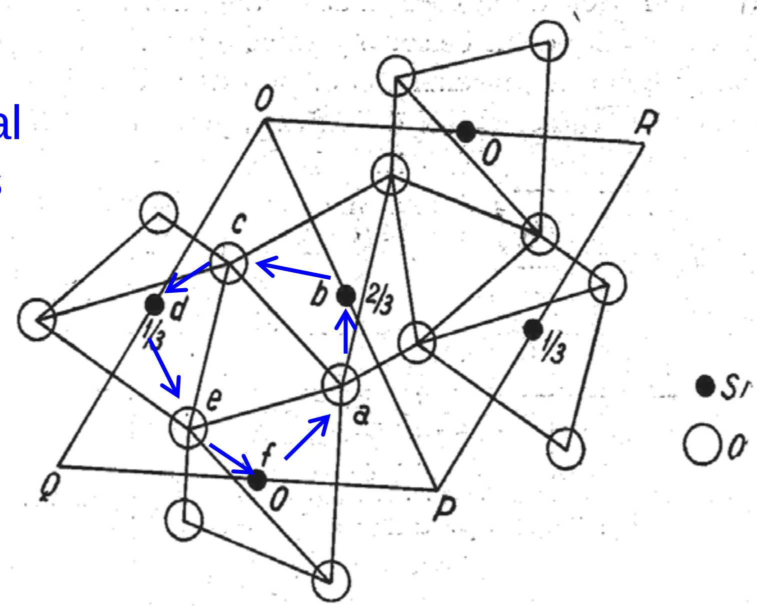


FIG. 7-15.—Cuarzo izquierdo. Rotación del plano de polarización con luz monocromática polarizada.

Supongamos que tenemos una estructura con fuertes enlaces formando una hélice en un sentido dextro. En este sentido la velocidad de un rayo de luz, que camine según el eje de la hélice, será



Estructura del cuarzo. Los tetraedros $[SiO_4]$ forman una espiral levógira *abcdef*.

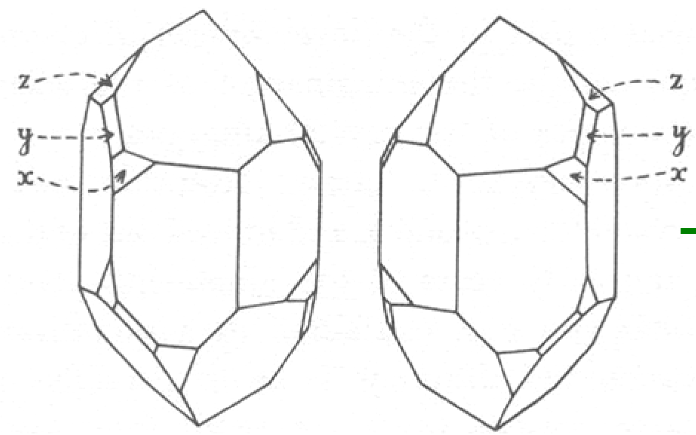
menor que la velocidad de la luz en el sentido levo. Por tanto, en el sentido de la hélice de enlaces habrá un retraso, que se manifiesta por el giro del plano de polarización de la luz.

Adapted from: J. L. AMORÓS (1958) *Cristalofísica*. Edt. Aguilar (p.174-175)

Symmetry & physical properties

The absence of a symmetry centre and the presence of a rotation axis with with integrated tanslation are crucial

$P\,3_1\,21$ (left) / $P\,3_2\,21$ (right) quartz crystals



Natural quartz crystal (α-form, symmetry class 32)

[by convention, levo-rotation is positive]

→ Quirality / Enantiomorphism

Provocative question: is there any possible relationship between the left- or right-handed character of pegmatitic euhedral quartz and eventual phenomena of magnetic N-S polarity inversion of the Earth's rotation axis along geological times?

The criation of Adam - Miguel Ângelo

"Asymmetry creates the phenomenon"

Pierre CURIE

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Piezoelectricity

Quartz was the first material recognized as owing this property

From: J.F. NYE, *Physical properties of crystals*. Clarendon Press, 1957

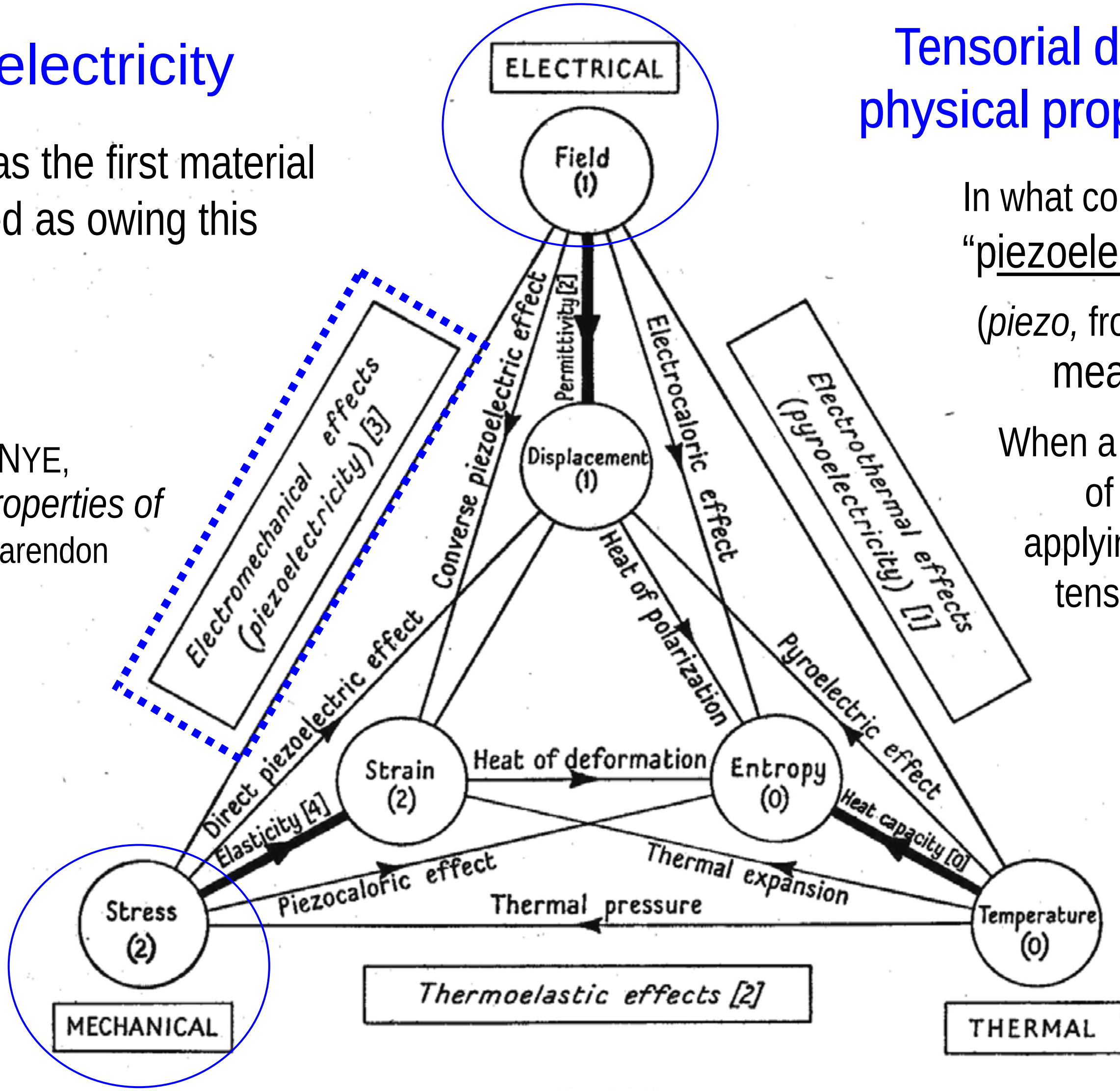


Fig. 10.1. The relations between the thermal, electrical and mechanical properties of a crystal, showing (*a*) the names of the properties and the variables, and (*b*) the corresponding symbols. The tensor rank of the variables is shown in round brackets and the tensor rank of the properties in square brackets.

Tensorial description of the physical properties of a crystal

In what consists the so-called "piezoelectric effect" ?

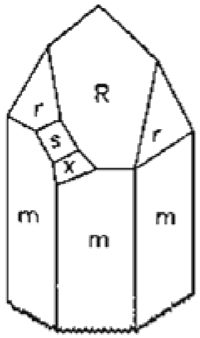
(*piezo*, from the Greek πιεζειν meaning *to compress*)

When a polar crystal is the object of an elastic deformation by applying a mechanical stress or tension, a polar momentum is developped

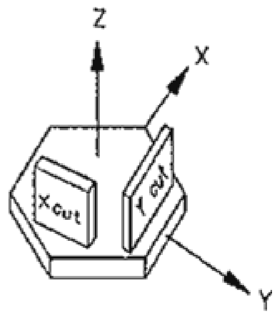
A piezoelectric crystal converts an applied stress into an electric current and vice-versa

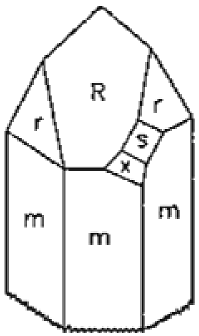
Development of an electric potential in a **quartz** single-crystal by elastic deformation

(aplication of a stress)



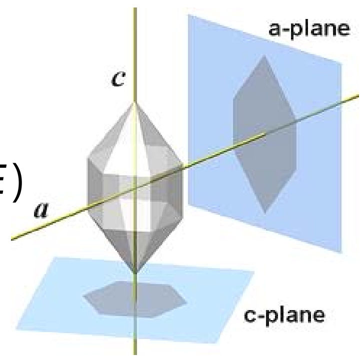
Letf-handed crystal

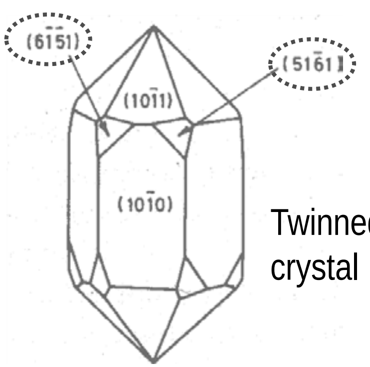




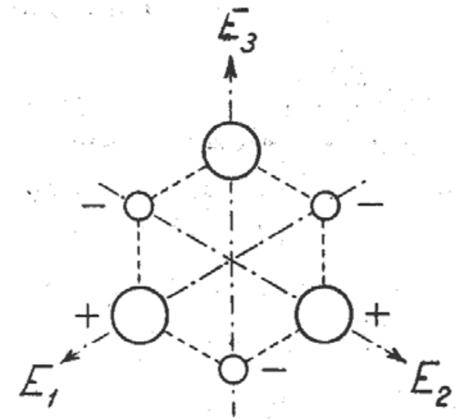
Right-handed crystal

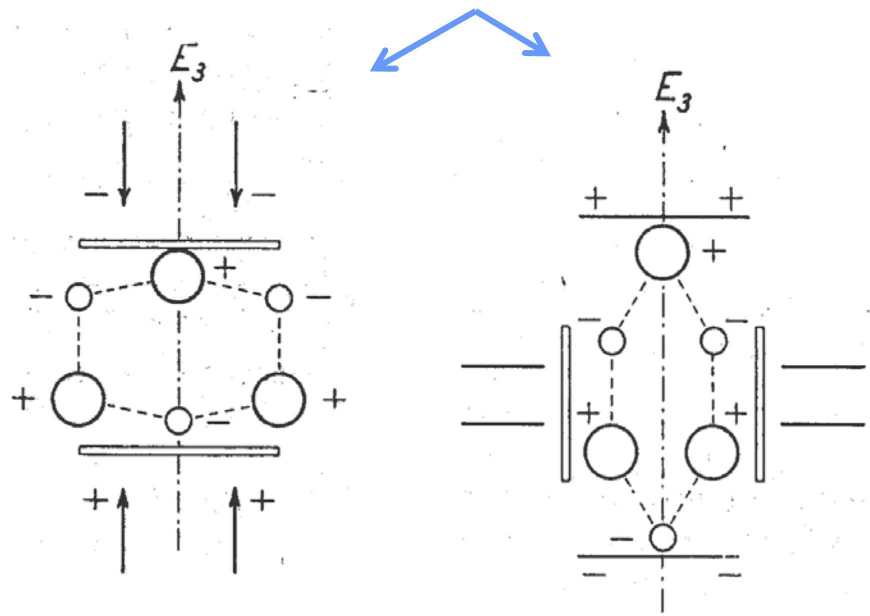
(*E*)





Twinned crystal





Adapted from: J. L. AMORÓS (1958) *Cristalofísica*. Edt. Aguilar (p.219)

Industrial quartz crystals with controled degree of purity

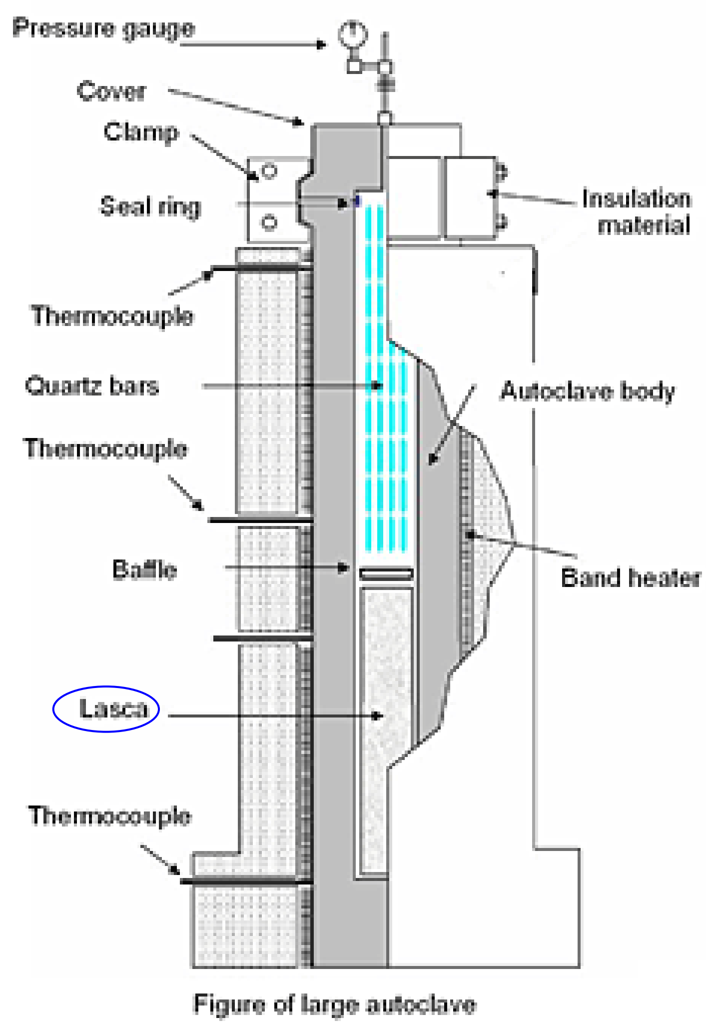
[*cultered quartz crystals*]

Natural crystals present various kinds of defects:

twinning, chemical impurities (either substitutional or by insertion) e inclusions (solid as well as fluid).

Quartz with less than 50 ppm of impurities (*high-purity quartz, HPQ*) is the raw-material for the **synthesis of electronic quality crystals** nowadays mainly produced in Japan, China, Russia and United States – that have originally (and up to the sixties) used natural crystals imported from Brasil and collected at Arkansas. The fragments of quartz from granite pegmatites had then the Portuguese designation of "*lascas*" conserved until today.

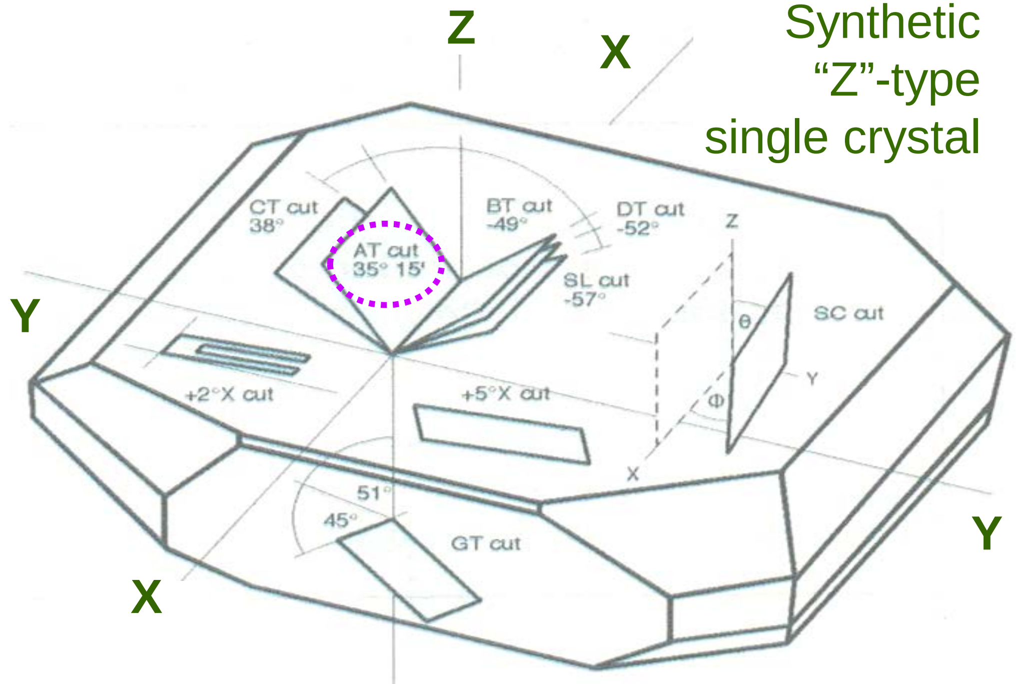
See: U.S. Geological Survey, Mineral Commodity Summaries (2011) 126-127.



Autoclave used in the synthesis of "cultured quartz crystals"

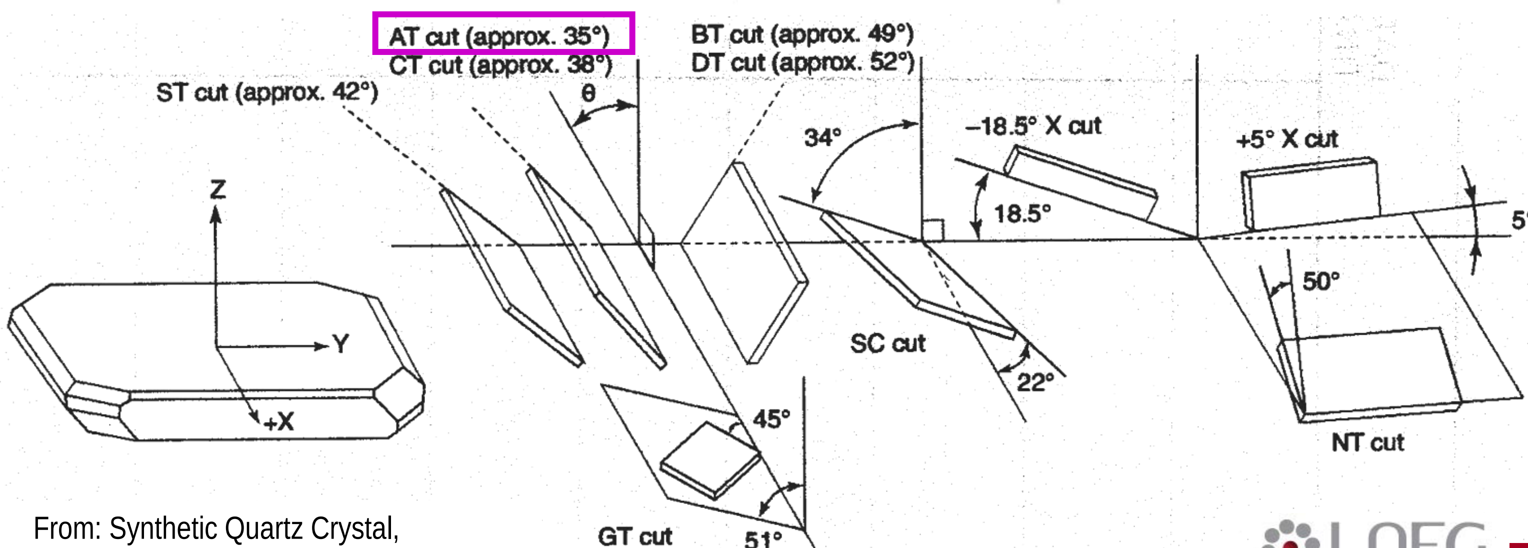
Industrial crystals are cutted from a synthetic single crystal along specific orientations according to the foreseen "high-tech" applications of final "cultured quartz crystals"

Synthetic "Z"-type single crystal



Cut orientation relatively to the crystallographic axes (X,Y,Z) of a "Z "-type single crystal

AT is the most common cut-type



From: Synthetic Quartz Crystal, Nihon Dempa Kogyo Co. Ltd

2010 U.S. NET IMPORT RELIANCE FOR SELECTED NONFUEL MINERAL MATERIALS

Commodity	Percent	Major Import Sources (2006-09)
ARSENIC (trioxide)	100	Morocco, China, Belgium
ASBESTOS	100	Canada
BAUXITE and ALUMINA	100	Jamaica, Brazil, Guinea, Australia
CESIUM	100	Canada
FLUORSPAR	100	Mexico, China, South Africa, Mongolia
GRAPHITE (natural)	100	China, Mexico, Canada, Brazil
INDIUM	100	China, Canada, Japan, Belgium
MANGANESE	100	South Africa, Gabon, China, Australia
MICA, sheet (natural)	100	China, Brazil, Belgium, India
NIOBIUM (columbium)	100	Brazil, Canada, Germany, Estonia
QUARTZ CRYSTAL (industrial)	100	China, Japan, Russia
RARE EARTHS	100	China, France, Japan, Austria
RUBIDIUM	100	Canada
STRONTIUM	100	Mexico, Germany
TANTALUM	100	Australia, China, Kazakhstan, Germany
THALLIUM	100	Russia, Germany, Netherlands
THORIUM	100	United Kingdom, France, India, Canada
YTTRIUM	100	China, Japan, France
GALLIUM	99	Germany, Canada, China, Ukraine
GEMSTONES	99	Israel, India, Belgium, South Africa
BISMUTH	94	Belgium, China, United Kingdom, Mexico
PLATINUM	94	South Africa, Germany, United Kingdom, C
ANTIMONY	93	China, Mexico, Belgium
GERMANIUM	90	Belgium, China, Russia, Germany
IODINE	88	Chile, Japan
RHENIUM	86	Chile, Netherlands
DIAMOND (dust, grit and powder)	85	China, Ireland, Russia, Republic of Korea
STONE (dimension)	85	Brazil, China, Italy, Turkey
POTASH	83	Canada, Belarus, Russia
COBALT	81	Norway, Russia, China, Canada
TITANIUM MINERAL CONCENTRATES	81	South Africa, Australia, Canada, Mozambique
SILICON CARBIDE	77	China, Venezuela, Netherlands, Romania
ZINC	77	Canada, Peru, Mexico, Ireland
BARITE	76	China, India
TIN	69	Peru, Bolivia, China, Indonesia
VANADIUM	69	Rep. of Korea, Czech Republic, Canada, Austria
TUNGSTEN	68	China, Canada, Germany, Bolivia
SILVER	65	Mexico, Canada, Peru, Chile
TITANIUM (sponge)	64	Kazakhstan, Japan, Ukraine, Russia
PEAT	59	Canada
PALLADIUM	58	Russia, South Africa, United Kingdom, Belgium
CHROMIUM	56	South Africa, Kazakhstan, Russia, China
MAGNESIUM COMPOUNDS	53	China, Austria, Canada, Brazil
BERYLLIUM	47	Kazakhstan, Kenya, Germany, Ireland
SILICON (ferrosilicon)	44	China, Russia, Venezuela, Canada
LITHIUM	43	Chile, Argentina, China
NICKEL	43	Canada, Russia, Australia, Norway
NITROGEN (fixed), AMMONIA	43	Trinidad and Tobago, Russia, Canada, Ukraine
ALUMINUM	38	Canada, Russia, China, Mexico
MAGNESIUM METAL	34	Canada, Israel, China, Russia
GOLD	33	Canada, Mexico, Peru, Chile
COPPER	30	Chile, Canada, Peru, Mexico
MICA, scrap and flake (natural)	27	Canada, China, India, Finland
GARNET (industrial)	25	India, Australia, China, Canada
PERLITE	25	Greece
SALT	24	Canada, Chile, Mexico, The Bahamas
VERMICULITE	22	China, South Africa
SULFUR	17	Canada, Mexico, Venezuela
GYPSUM	15	Canada, Mexico, Spain
PHOSPHATE ROCK	15	Morocco
IRON and STEEL SLAG	10	Japan, Canada, Italy, South Africa
CEMENT	8	China, Canada, Republic of Korea, Taiwan
IRON and STEEL	7	Canada, European Union, China, Mexico
PUMICE	7	Greece, Turkey, Iceland, Mexico
DIAMOND (natural industrial stone)	3	Botswana, South Africa, Namibia, India
LIME	2	Canada, Mexico
STONE (crushed)	1	Canada, Mexico, The Bahamas

Potential markets for "lascas"

USGS
science for a changing world

2006 U.S. Net Import Reliance For Selected Nonfuel Mineral Materials

Commodity	Percent	Major Import Sources (2002-05)
ARSENIC (trioxide)	100	China, Morocco, Mexico, Chile
ASBESTOS	100	Canada
BAUXITE and ALUMINA	100	Jamaica, Guinea, Australia, Brazil
COLUMBIUM (niobium)	100	Brazil, Canada, Estonia, Germany
FLUORSPAR	100	China, Mexico, South Africa, Mongolia
GRAPHITE (natural)	100	China, Mexico, Canada, Brazil
INDIUM	100	China, Canada, Japan, Russia
MANGANESE	100	South Africa, Gabon, Australia, China
MICA, sheet (natural)	100	India, Belgium, China, Brazil
QUARTZ CRYSTAL (industrial)	100	Brazil, Germany, Madagascar, Canada
RARE EARTHS	100	China, France, Japan, Russia
RUBIDIUM	100	Canada
STRONTIUM	100	Mexico, Germany
THALLIUM	100	Russia, Belgium
THORIUM	100	France
VANADIUM	100	Czech Republic, Swaziland, Canada, Austria
YTTRIUM	100	China, Japan, France, Austria
GALLIUM	99	China, Japan, Ukraine, Russia
GEMSTONES	99	Israel, India, Belgium, South Africa

Since 2002 the United States import the crystals for high-tech applications from Brasil, Madagascar, Germany and Canada until 2005 and thereafter from China, Japan and Russia

The industrail relevance of synthetic quartz crystals in producing countries is such that an association focused on that objective was created in Japan:

QIAJ, *Quartz Cryst. Assoc.*

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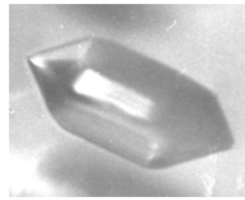
Defects & Impurities

50 μg.g^{-1} is the maximum content of trace elements in *HPQ*

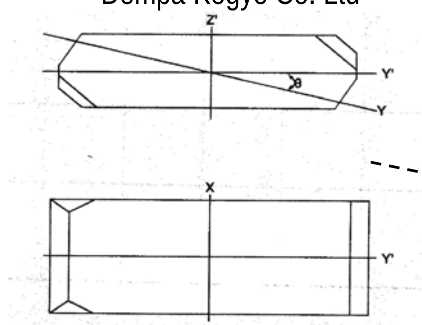
Al, **Li**, **Na**, **H** are the most common ***natural chemical** impurities in primary, magmatic quartz from pegmatites*:

Al^{3+} ions replace Si^{4+} in [SiO_4] tetrahedra and the charge difference is compensated by the insertion of mono-valent ions Na^{+} and Li^{+} along channels built by the chains of tetrahedra along the *c* axis of the crystal and by the creation of hydroxyls, (OH^{-}). When exposed to an ionizing radiation, Al-M^{+} centres give rise to a mixture of Al vacancies (*Al-holes*) and Al-OH^{-} centres (active in the infrared spectral region). These impurities are not removed through the synthesis in autoclave and hinder the use of the produced *cultured quartz crystals* in optronics

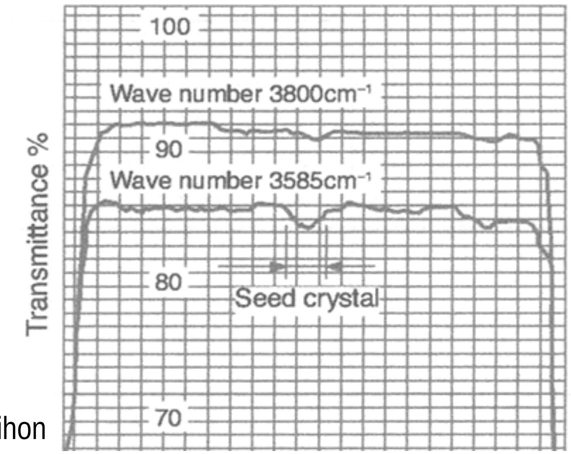


A "negative crystal", the unique tolerated defect...

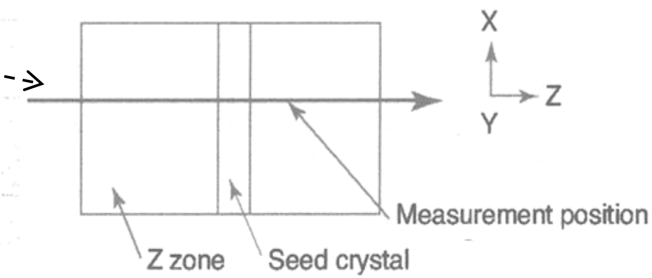
From: Synthetic Quartz Crystal, Nihon Dempa Kogyo Co. Ltd



Evaluation of the quality factor "Q" of a synthetic crystal



Transmitance of infrared radiation with two wavelenghts



Cross section of lumbered synthetic quartz crystal (Pure-Z)

See e.g. "**Quartz crystal, the timing material**"
http://www.4timing.com/techquartz.htm

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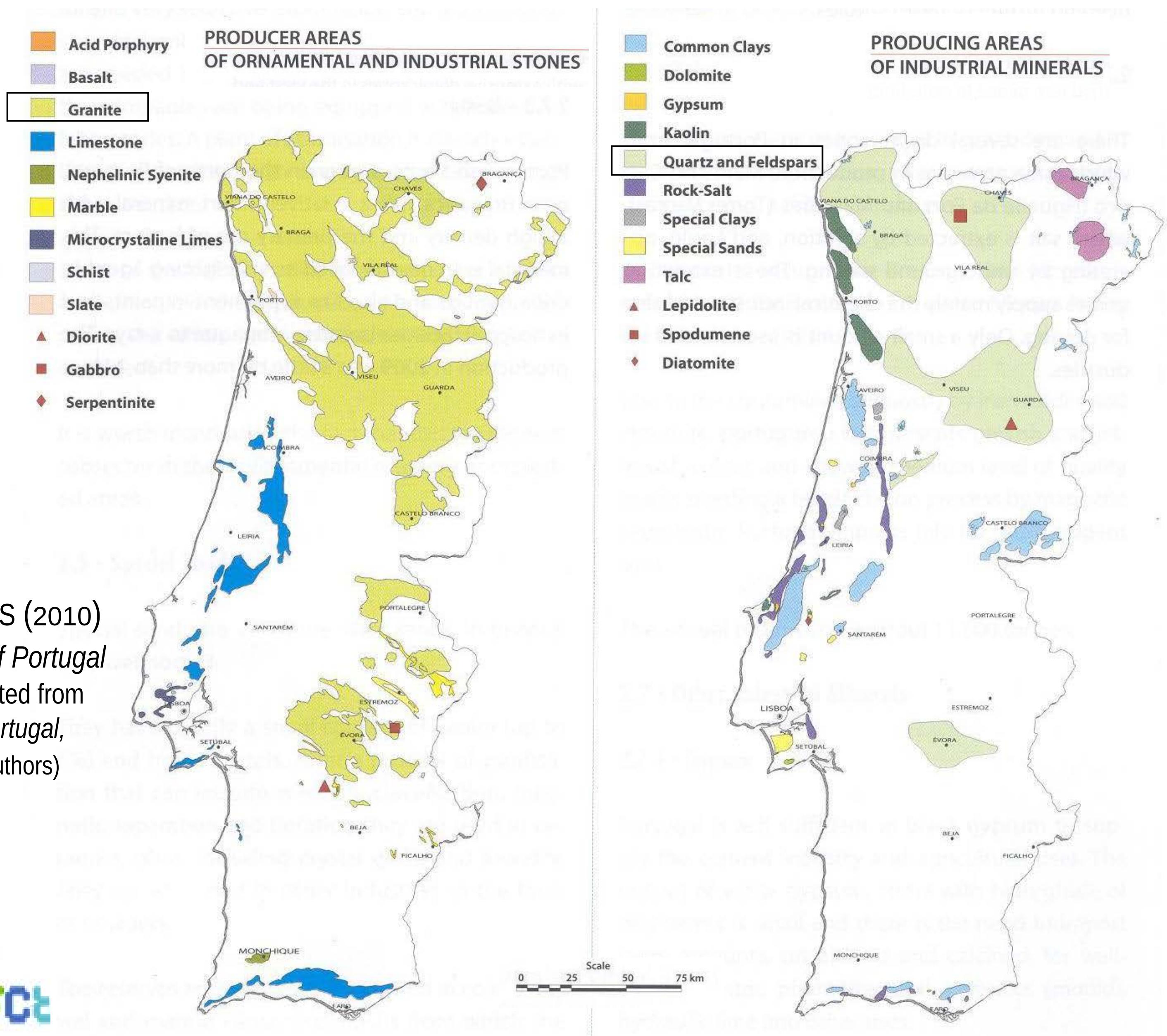
Quartz / granites in Portugal



From: L.P. MARTINS (2010)
Mineral Resources of Portugal
Edtion of DGEG adapted from
Mineral Potential of Portugal,
IGM, 1998 (various Authors)

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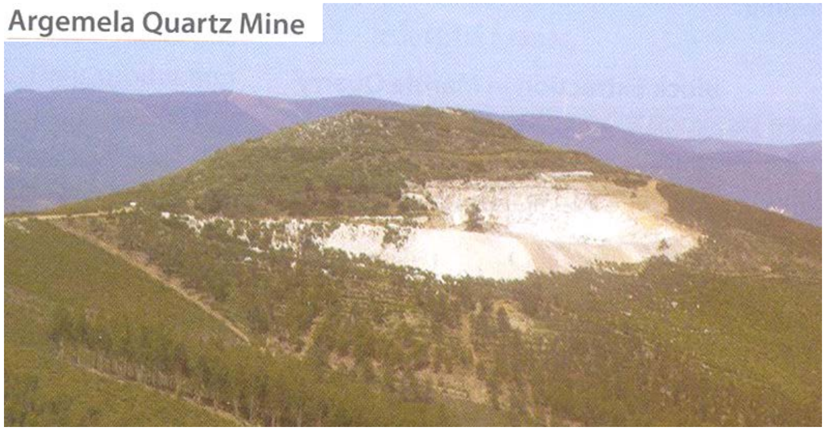
Argemela Quartz Mine



Bajoca Quartz and Feldspar Mine

De: L.P. MARTINS (2010) *Mineral Resources of Portugal*. Edição DGEG

Ornamental granites (that includes similar rocks, such as slate, acid porphyry, serpentine, nepheline syenite, witch had a small production) represent the subsector with the highest growth rate in recent years, and the production achieved in 2007 puts it in the first place, ahead of the marbles and limestones, with 24% of the global value production.

The global reserves of granites are very large and further detailed studies in some areas are needed.

1.2 - Industrial Stones

. . .

1.2.1 - Use of Quarrying Wastes

_ From granites and similars

Granite wastes have the highest rate of utilisation. The most common use is the production of cobblestones for paving. This use is an important subsidiary industry with a large incidence in foreign markets. These wastes are also used for masonry and other purposes.

Possible export of quartz fragments (*taliscas/lascas*) as a valuable raw material to produce synthetic quartz crystals

Summarizing: World resources of natural quartz crystals appropriate for a direct application in optoelectronics are scarce or even minute, but the search for synthetic quartz crystals is still raising, thus improving the added-value of *lascas* from natural crystals with suitable chemical characteristics to produce cultured quartz crystals.

Grata pela atenção dispensada !

Laboratório Nacional de Energia e Geologia, I.P.

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