

SYNTHETIC ALEXANDRITE, MORE MAGIC THAN RUBIK'S CUBE

Alberto Malossi

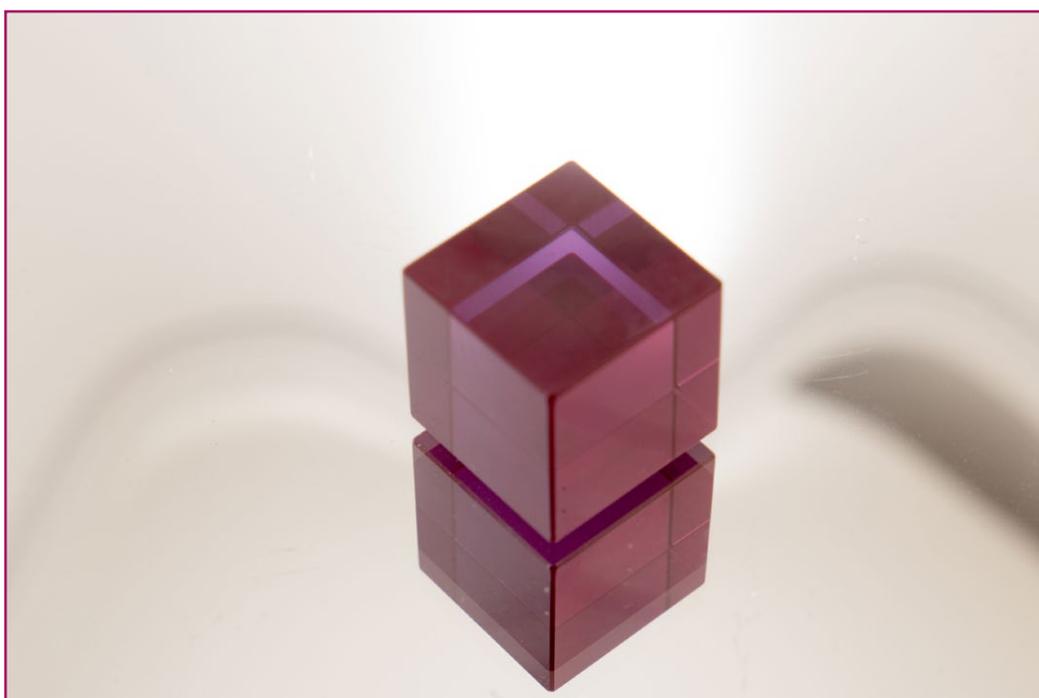


Fig. 1 Test cube. (Photo: Alberto Malossi)

Introduction

It all started with a cube. If we talk about Alexandrite we immediately think of its color change, of those trivalent chromium ions replacing the Aluminum ones in the host crystal, allowing the color variation in accordance with the wavelength of light: green/blue under natural light and red/purple under artificial light. Every gemologist knows that. But multiplying the effect - and the magic - thanks to tricoism and UV rays, to obtain a wider range of clearly visible and differentiated colors, is a truly unique experience.

For the purpose a cube of synthetic Alexandrite was enough. It was a cube for laser use measuring 20 mm by the side, cut with faces perpendicular to the axes,

photographed with a macro lens, polarizing filter and an adjustable light source, from a minimum of 2,500 °K to a maximum of 10,000 °K.

Three extreme absorption values, three different colors for each metameric variation, in total six colors plus a changing red under UV rays. The three colors follow the orientation of the three main spatial axes, red on the **X** axis facing the observer; orange on the **Y** axis parallel to the observer and green on the **Z** axis, the vertical axis of growth.

Three series of unpublished photos: in the first we can see a single color, when the observation point is perpendicular to the face; in the second it is perpendicular to the side and two colors are visible; in the third it is perpendicular to the edge, and we see three colors. If we consider that the colors of the images have not been altered, neither the basic ones nor the intermediate ones, it is worth noting that its bandwidth is actually exceptionally extended.

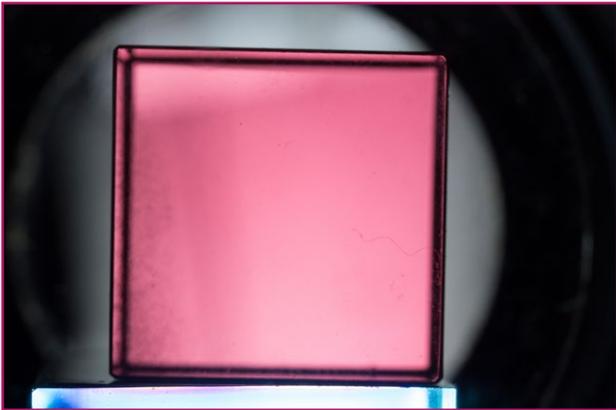
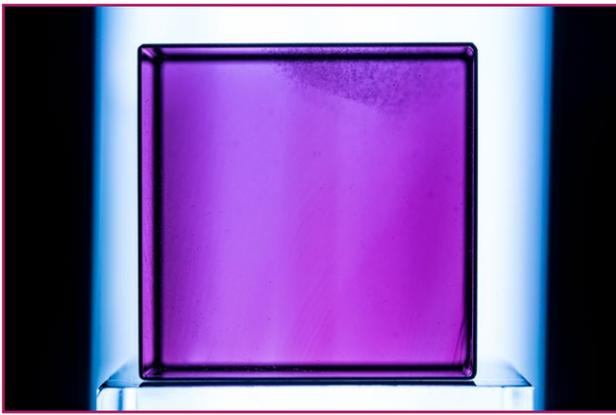


Fig. 2-9 A face of the cube. Different colors according to the orientation of the 3 main spatial axis. (Photo:Alberto Malossi)

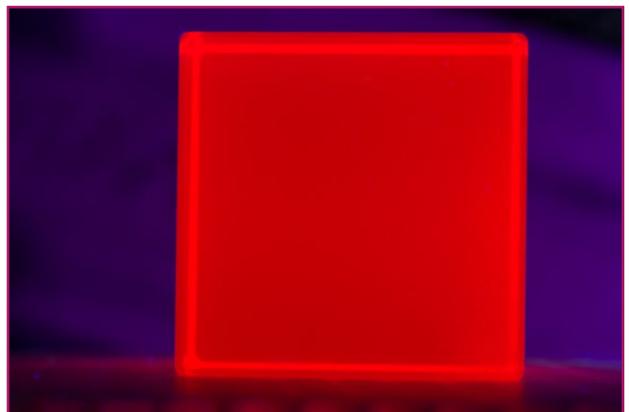
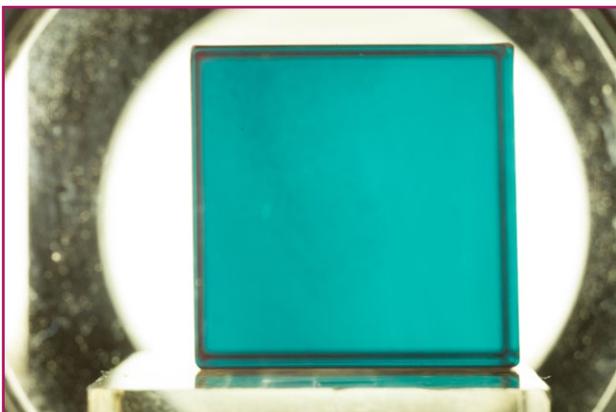
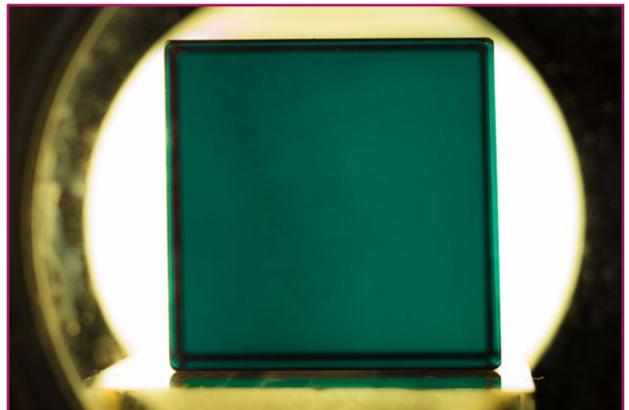
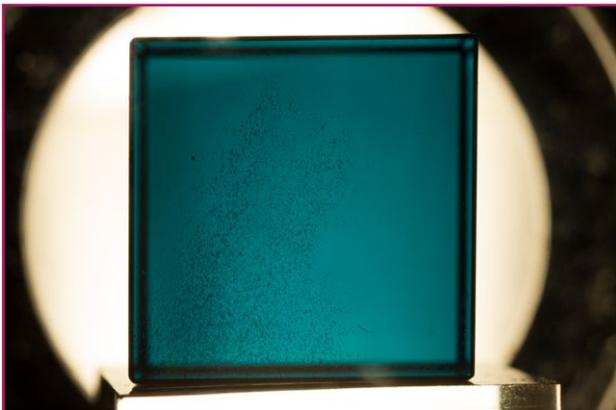
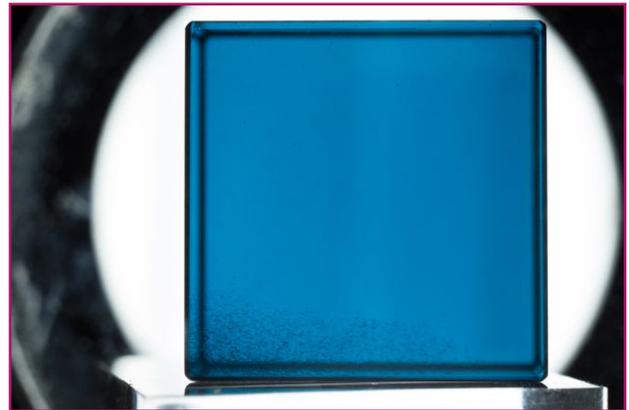
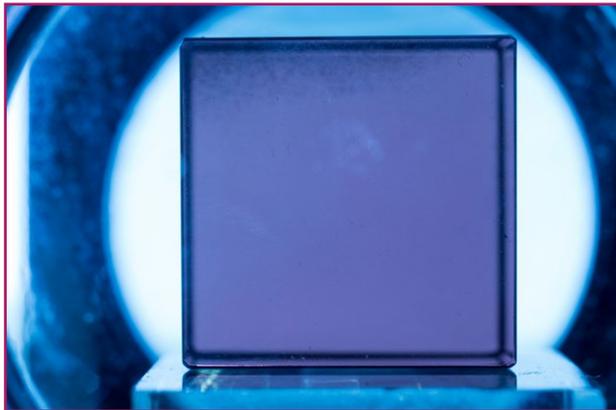
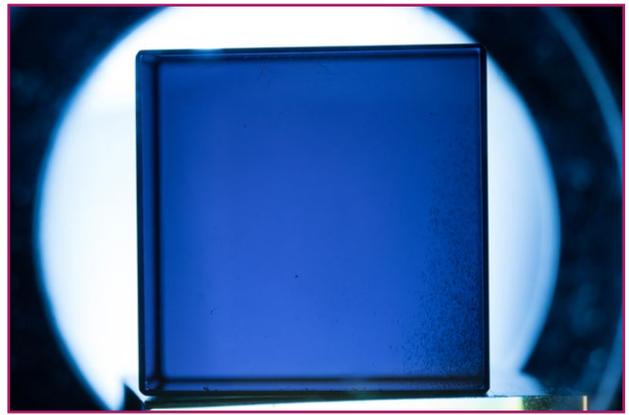
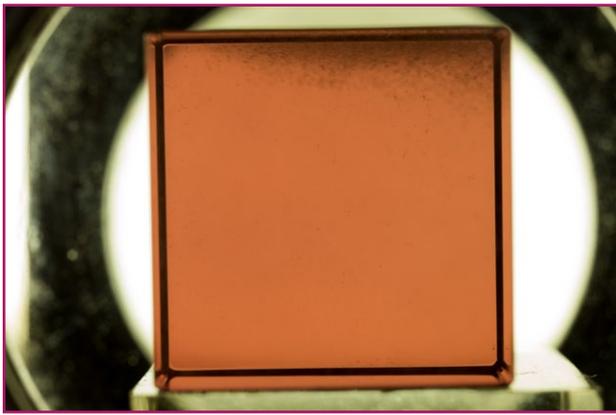


Fig. 10-17 A face of the cube. Different colors according to the orientation of the 3 main spatial axis. The last one is an ultraviolet face. (Photo: Alberto Malossi)

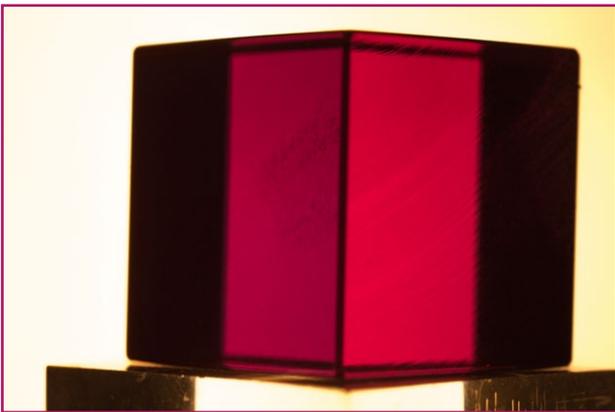
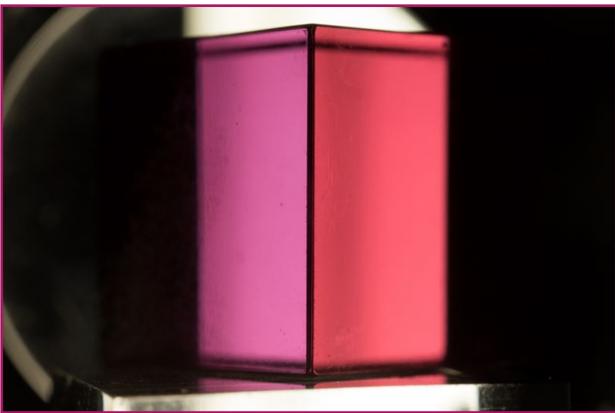
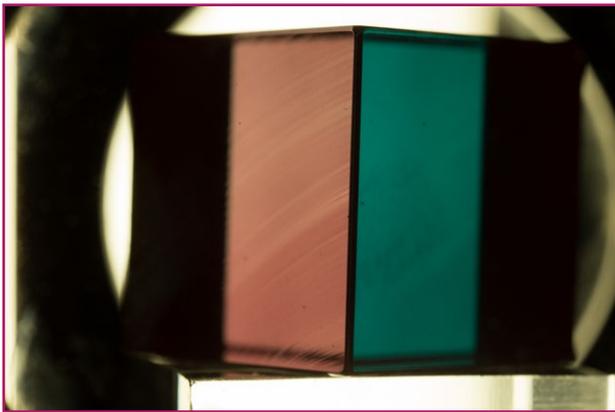
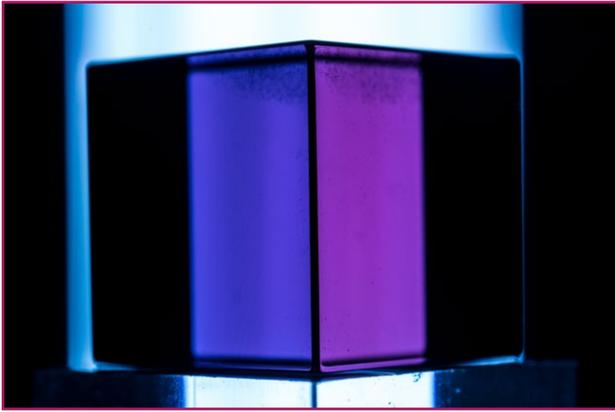


Fig. 18-24
Two sides of the cube. (Photo: Alberto Malossi)

Alexandrite is indeed a gorgeous gem. No wonder that in the years following its discovery - occurred in 1830 in the Urals in the Tokowaia emerald deposit by the mineralogist Nordenskjöld - the European bourgeoisie and aristocracy rushed to buy it and, naturally, this encouraged the scientists of that time to carefully study alexandrite in an attempt to reproduce it synthetically.

The history

It was in fact in 1845 that **J.J. Ebelmen**, a renowned French chemist, synthetically reproduced Alexandrite in small millimeter crystals, using a flux mixture of sodium borate with BeO , Al_2O_3 , natural alexandrite powder and $\text{K}_2\text{Cr}_2\text{O}_7$ as a source of chromium.

Later, in 1858 **Deville and Caron** obtained crystals of chrysoberyl from Al and Be fluorides always in a borax flux, and in 1888 **Hautefeuille and Perrey** produced them with a different flux, based on alkali sulphates and sodium carbonate.

After the initial enthusiasm, the scientists focused on better known and more requested synthetic materials such as Ruby and Emerald, making synthetic Alexandrite just a laboratory curiosity; meanwhile, since the Russian deposits had almost run out, commercial concern with the natural stone decreased, turning it into just a rare stone for collectors.

A long oblivion followed until 1964, when two American scientists, **E.F. Farrel and J.H. Fang** presented in the "*Journal of the American Ceramic Society*" a thorough research aimed at obtaining crystals as small as 3 mm from a flux based on molybdenum trioxide and lithium molybdate (but it was not exactly a novelty, since the lithium molybdate had already been used in 1888 by Hautefeuille in the synthesis of the emerald, but the crystals were larger).

In 1969 **D. Rykl and J. Bauer**, both from East Germany, succeeded in producing chrysoberyl through a hydrothermal synthesis from a mixture of BeO and Al_2O_3 , using as a solvent Sodium NaOH hydroxide, but no commercial applications followed.

Following the discovery of its laser properties, the gemological and scientific interest in synthetic Alexandrite grew to become commercially viable for the first time in 1973 with the **Creative Cristal inc.**, California, USA, which produced large crystals grown in a flux based on molybdenum trioxide MoO_3 and lithium oxide Li_2O in a platinum crucible.

Transparent gem quality Alexandrites showing an excellent color change were obtained and introduced into the market under the trade name "*Alexandria-Created Alexandrite*"; later in 1975 the first Czochralski method for the creation of Alexandrite boules apt to obtain the first laser rods was licensed. In 1974 Alexandrite was also produced with a chatoyancy effect, but it was never put

on the market.

The challenge was set and the evolution was going to be frantic, the modern adventure of synthetic Alexandrite had begun!

In 1976 the **American Allied Corporation** began to market it to be used as laser rods, always produced under the Czochralski method; since for this use high quality clean material is required, production leftovers became available, sold to be used as gems.

In 1978 **Seiko** started the production of synthetic Alexandrite for scientific purposes through the zonal fusion method and in 1983 it deposited a "cat's eye" quality production patent simultaneously with **Sumitomo**; two years later, in 1980, the Japanese **Kyocera Corporation** began producing it using both flux and Czochralski methods and put it on the market under the name of "*Inamori Created Alexandrite*" modified in the USA in "*Crescent Vert Alexandrite*"; in 1986 the company also produced the "cat's eye" quality.

Also in the 1980s, the Russian productions of synthetic Alexandrite for the market of gems by the Russian-Thai company **Tairus** began, using various innovative and unique methods, studied by the scientists of the Institute of Geology and Geophysics of the Russian Academy of Sciences department of Novosibirsk.

In Russia the manufacture of synthetic Alexandrites produced through several procedures such as flux, hydrothermal and gas transport (*Rodionov and Novgorodtseva, 1988*) methods, along with horizontally oriented crystallization (*Gurov 2003*) intensified, but mainly thanks to the improved Czochralski method, the most suitable for the production of high quality laser rods.

After the discovery in the state of Minas Gerais in Brazil in 1987 of the Hematite deposit of Alexandrite, the largest in the world, from which high-quality gemstones in terms of transparency and color change were sourced, the interest of the jewelry sector grew considerably, stimulating in turn the production of synthetic Alexandrite.

Currently Alexandrite for gem use is produced exclusively in Russia with the Czochralski method by a small community of "growers" connected to **Tairus** which markets it worldwide, "renamed" under various brands.

But other abundant gemological material comes from the rod production waste generated by a few companies, not more than 4 in the world.

And here the story becomes engaging, because one of the mythical "growers" of synthetic Alexandrite, Maurilio Guerini, an international consultant, and "master" of the Czochralski method (he introduced new and remarkable growth methods), sharing with the author of this article the same passion for synthetic gems, allowed a real-time exciting update and made accessible technical aspects and unpublished images of this synthesis about which too little is said but can reveal many interesting things.

Jacques-Joseph Ebelmen, the first one

His name appears at the first floor of the Eiffel Tower: he was immortalized, among other 72 scientists, for his undisputed brilliance. He was the first creator of synthetic gems thanks to his sharp intuitions, which range from understanding that crystal, both natural and synthetic ones, can form and grow at temperatures much lower than those of its fusion if supported by a “solvent fluid”, to considering the possibility of forming crystals through vapor deposition (confirmed, after 150 years, by the production of synthetic Moissanite and CVD synthetic diamonds).

Jacques-Joseph Ebelmen, born in Baume-les-Dames (Doubs) in 1814, can be considered the founder of the science of synthetic gems. Thanks to his studies at the Ecole Polytechnique (and later at the Ecole des Mines, where he was appointed assistant professor of industrial chemistry) and also to his experience as a mining engineer at the manufactures of Sevres, he was able to exert a considerable influence on artistic, scientific and industrial development of porcelain manufacture, metal fusion and earth science, counting on his knowledge of the chemistry of mineralization and of high temperature chemical reactions, such as those forming synthetic gems.

By discovering how rocks are altered and modified and how minerals are formed, he was the first to guess that gas in the atmosphere affects the rocks and the environment and unconsciously laid the foundations for modern environmental science. As a matter of fact, he was the first scientist to imagine that the atmosphere is modified by living beings, the first to show that it is possible to obtain by man-made chemical synthesis the minerals and gems of the earth and many other types of compounds that are missing in the classification of crystallized minerals.

Not only. Ebelmen theorized and invented the first and rudimentary “flux method” in history (based on boric acid) reproducing this way small crystals of many minerals: white, pink and black Spinel, chrome and native iron, Alexandrite chrysoberyl, Emerald, Peridot and Hyaline Corundum in hexagonal laminar crystals. He also created many crystalline compounds not occurring in nature, such as aluminates and metal chromites.

All works, memories and notes of Ebelmen were collected posthumously, in 1855, in two volumes, constituting a fundamental source of inspiration and valuable scientific information for later scientists.

He died in Paris on March 31, 1852, at thirty-eight, for brain fever.



Fig. 32 A portrait of Ebelmen.

Synthesis methods

Synthetic Alexandrite and Chrysoberyl can be grown in different ways, through fusion under Flux, Czochralski, Verneuil, Bridgman and Zonal Fusion processes as well as through hydrothermal and vapor deposition methods. There are many procedures but most of them are merely experimental, while the ones traditionally used by the industry are only three.

1) The flux method

Theorized and experimented by Ebelman the “fluidization mixture”, in short called “flux”, is used to melt another material with a much higher melting point (the nutrient).

It was masterly used by Carrol Chatham in 1936.

Today it has completely fallen into disuse, because it is not possible to produce perfectly pure, large and homogeneous crystals with precise optical and physical characteristics for industrial use.

In the case of synthetic Alexandrite, mainly two nutrients are used, aluminum oxide (Al_2O_3) and beryllium oxide (BeO) and - depending on the mixture - as dopants for color change Cr (Cr^{3+}), V, Fe and, less commonly, Mn, Co, Ni, W, and Ce are used.

Ti, Sn, and Ge Oxides have been used to cause the “chatoyancy” effect.

Depending on the composition of the flux, the growth temperature varies from 1,100 °C to 1,300 °C, the crystallization occurs either by spontaneous nucleation or by insemination with natural or synthetic Chrysoberyl, or with Alexandrite, mostly in a platinum crucible.

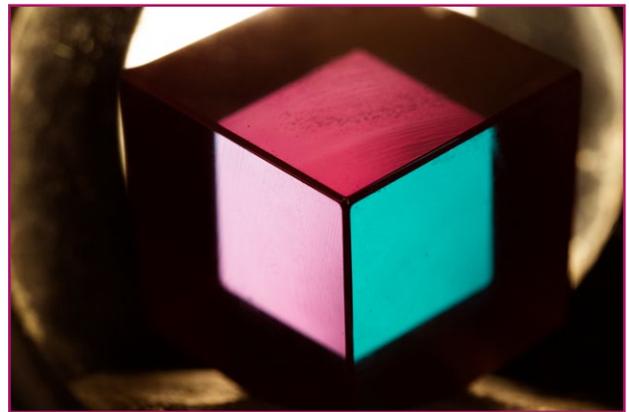
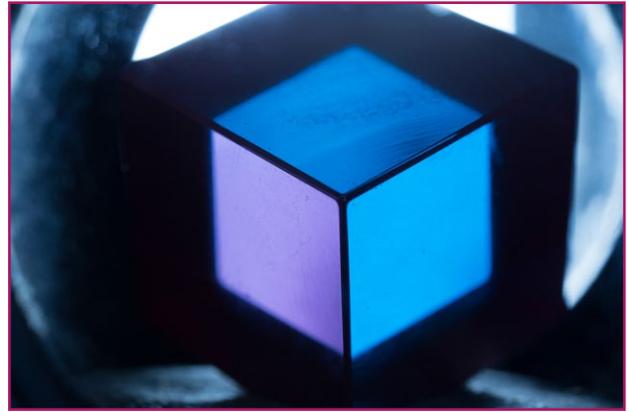
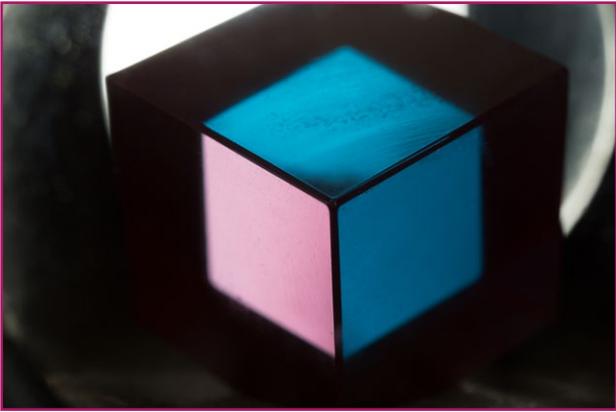
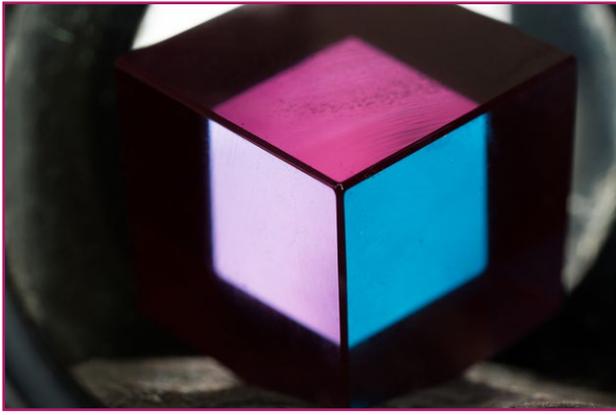
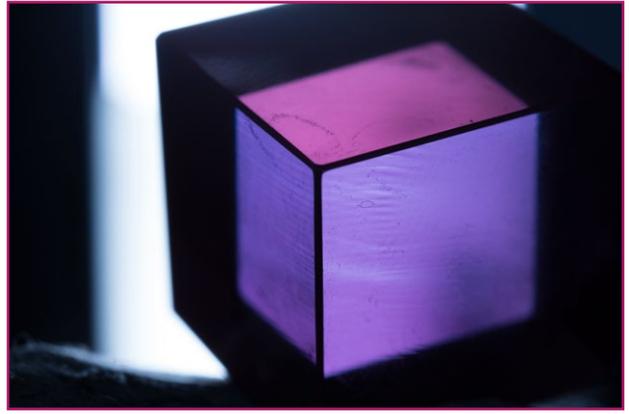
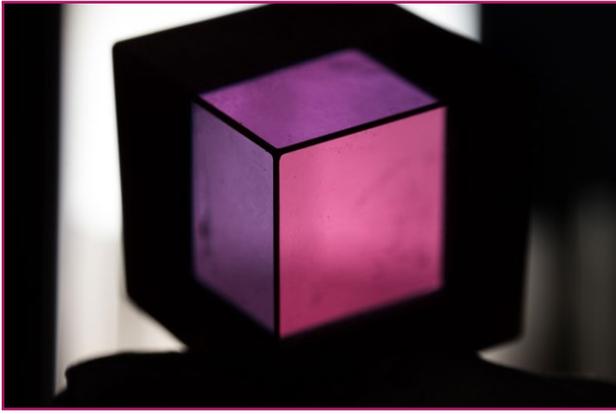


Fig. 25-31
Three faces on the edge. (Photo: Alberto Malossi)

The substances most historically used to compose the flux are Li_2MoO_4 Lithium Molybdate, Molybdenum trioxide MoO_3 , Bismuth oxide Bi_2O_3 , V_2O_5 Vanadium pentoxide, but there are many others, and of course every manufacturer has its own jealously guarded secret formula.

At the turn of the 70s/80s, a variant of the flux method developed in Russia - originally used by the Novosibirsk Academy of Sciences - based on the "thermal gradient", which is based on high temperature at the bottom of the crucible to dissolve the nutrient and a less elevated temperature, subject to cooling, in the upper part. The temperature difference provokes a convective motion allowing the Alexandrite to crystallize on crystalline seeds placed in the lower and warmer part.

This system was also conceived to operate in a "reverse" mode, warm on top and cold on bottom, allowing at the same time both spontaneous growth and seed growth, after placing a seed on the bottom of the crucible.

Generally spontaneous nucleation crystals are smaller than those obtained from insemination, and in any case do not exceed 5/6 cm.

2) The zonal fusion method

This method uses only compressed and sintered powdered nutrients in the shape of a long rod of a few cm in diameter. At one end a seed crystal is placed and the whole is placed vertically in a particular induction furnace which heats the rod in a very restricted area, starting from the one where the seed is placed; the crystal is gradually dissolved. **Seiko** has invented a slightly different version where the heating source is generated by infrared rays focused by ellipsoidal reflectors. Also this method is no longer used for industrial purposes.

A derivation is the method of "horizontally oriented crystallization or MOC", a technique invented by

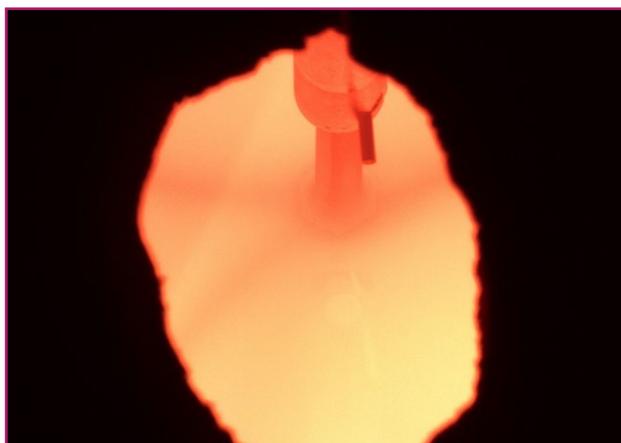


Fig. 33 Boule formation in the crucible. (Photo: Maurilio Guerini)

Bagdasarov in 1964 which allows the creation of larger crystals for laser use adopting cheaper containers made of Tungsten instead of Iridium (in the bibliography the description of the method can be found). This method is still utilized industrially for particular uses, given the unusual shape of the raw crystal.

3) The Czochralski fusion method

Currently this is the most widespread technological method because it takes into account the evolution of practice and technology and allows a perfect balance of the dopants according to their use.

It is also known as "traction technique" because the crystal is slowly extracted from a fused nutrient mixture. The starting material ($\text{Al}_2\text{O}_3 + \text{BeO} +$ various dopants) is perfectly mixed, sintered into circular pads and melted by induction into an Iridium or a Molybdenum crucible at a temperature of 1,857 °C under an insulating bell in an inert gas atmosphere; insulation is essential because beryllium is very poisonous, historically many researchers have suffered harmful consequences.

In the spindle an iridium rod is immersed at the end of which a bar of synthetic Alexandrite (obtained from a boule of the same composition) has been placed, triggering the growth of the crystal, which - as the picture shows - at the beginning is perfectly hexagonal rounding up its angles at the end due to the effect of surface heat radiation, as it grows across the crucible walls.

In the most advanced plants the development of the "monocrystal" (a single bulky crystal) - weighing about 3 kg - takes place in fifteen days, with a growth of about one millimeter per hour.

The shaft rotates at a speed of about 10 RPM. The centrifugal rotation supports specific metastable conditions for growth, nutrient mixing, temperature stabilization and convective motions so that the molten chrysoberyl remains in the optimal crystallization phase.

Near the center, where the centrifugal force is equal to zero, the conditions change, an unstable zone is formed, the spindle cools, the nutrients circulate very slowly favoring the formation of bubbles and small isolated crystals, oriented according to the growth axis C.

The chemical-physical reactions of the crystal formation process are very elaborate and complex because crystallization occurs in two phases, alpha and beta BeAl_2O_4 , therefore reference must be made to specific studies on the subject (see in the bibliography Gurov & Tsvetkov, 2008).

The formation of the typical zoned bands that start and radiate from the center, are due to the complex

temperature and nutrient fluctuations that all contribute to the wonderful transition between liquid and solid phases in which the “brick” constituting the crystalline building is formed.

Currently the production of synthetic Alexandrite for gem use occurs only through the Czochralski method which can be referred to two types of production:

1. production for exclusive use as gems, of intense color; with a strong color change and a percentage of Chrome variable between 0.35/0.40%: it is obtained thanks to simple, not very sophisticated plants, and without rotation of the so called “iridium drawing rod” where the hexagonal crystal grows similar to a spatula, given that the axis B is almost double in comparison with axis A (the axis C is used for draft) and inclusions are rarely found;
2. production deriving from the waste of the synthetic Alexandrite boule created to obtain laser rods, in which the percentage of Chrome does not exceed 0.13%, the color is lighter; the color change is always very strong, but the intensity of the color is lower. The boule is roundish and the inclusions are confined around the growth axis C.

A small digression follows to understand how laser rods are manufactured: from the boule, through the core drilling, the rods for laser use are obtained and subsequently treated by a particular and patented thermal process called “annealing” which eliminates the defects of the crystalline lattice of the single crystal, the metallic impurities, and all the other substances that would compromise the operational durability. This is how this how the growth lines are made not visible.

The gemological characteristics, variable but not too much

The gemological analysis of the synthetic Alexandrite is not discussed here, since the subject has been substantially dealt with in various studies, publications and researches started since the 1960s, although in recent years it seems there is a void.

But perhaps it can be interesting to summarize the main chemical-physical characteristics of synthetic Alexandrite which, of course, are subject to a certain variability and slightly differ from those of the natural equivalent (Table 1).

An (un)certain identification

Alexandrite, both natural and synthetic, is not a common gem and rarely happens to be certified; the identification of its origin can be very complex and sometimes uncertain.

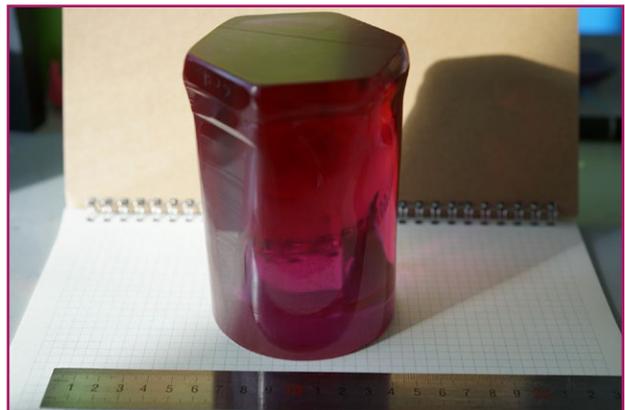


Fig. 34-36 A finished boule. (Photo: Maurilio Guerini)

The various methodological techniques and related data are not mentioned here because they are widely described in various studies by talented gemologists (Trossarelli, 1986; Pohl, 1989; Henn, 1992; Schmetzer et al. 1996; Anna-Kathrin Malsy [Gubelin lab.] 2011). The problem, however, is that these studies are dated and partial, because they refer to synthetic Alexandrite produced with synthesis now in disuse, perhaps from old Czochralski plants with growth without rotation and with spatular crystals easy to recognize from inclusions, from growth lines (when present) and from trace heavy metals in the chemical composition.

Table 1 - Synthetic Alexandrite: gemological characteristics

Chemical formula	BeAl ₂ O ₄ + Cr ³⁺ in traces
Indicative composition	Beryl 7.10% Aluminum 42.10% Oxygen 50.40% Chrome 0.40% Various trace impurities (Fe, V, Ga, Mg, heavy metal)
Crystal system	Orthorhombic (2/m2/m2/m)
Hardness	8.5 Mohs scale
Density	3.71 -3.73 g/cm ³
Refraction Indexes	n _α = 1.746; n _β = 1.75; n _γ = 1.755 - 1.76 double biaxial
Double refraction	0.009 (+/- 0.002)
Pleochroism	Intense, strong trichroism (X= purplish red, Y= orange, Z= green)
Fluorescence	- under long and short wavelength UV rays: very intense red, transparent - under X-ray: very intense red, those produced with the Czochralski method
Luster	Vitreous
Melting point	1.870 °C



Fig. 37 Inclusions along the growth axis C. (Photo: Maurilio Guerini)



Fig. 38-39 Crystal head in natural and artificial light where a perfectly hexagonal growth of the single crystal can be noted. (Photo: Alberto Malossi)

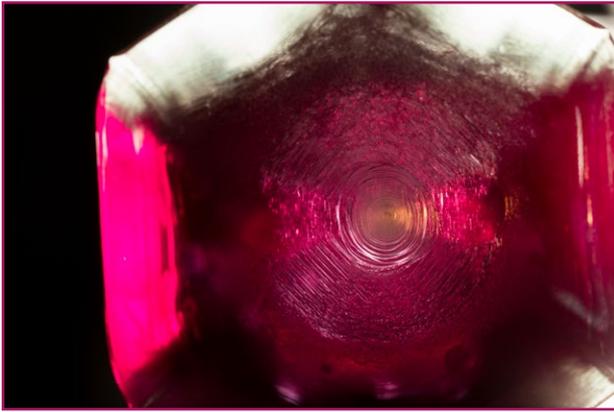
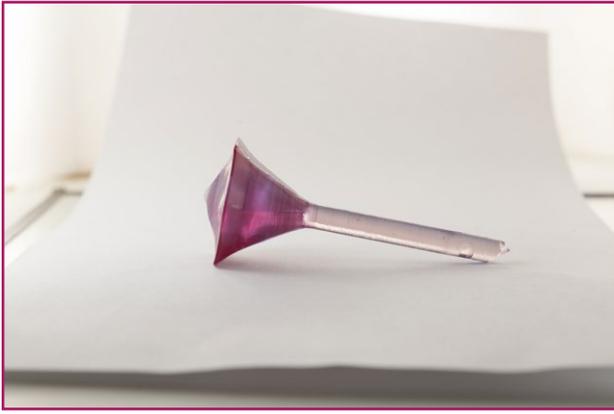


Fig. 40-43 This series of photos is exclusive because for the first time the initial formation of the crystal from a bar of synthetic Alexandrite is observed. The finding is the result of an "accident" that occurred at the plant, a trivial power failure, interrupting the growth at the beginning, freezing its crystalline aspects. Very interestingly, the growth of the crystalline building occurs, brick by brick (or rather crystal by crystal) starting from the center and then radiating. At the center we note the initial depigmented liquid phase which then crystallizes in a graduated way towards the periphery of the crystal... magnificent! (Photo: Alberto Malossi)

No information instead of new gemological researches on synthetic boules grown Alexandrite developed in modern plants are available, with reference to the gems obtained from the residual material after the coring process to produce laser rods, especially those coming from material treated with the "annealing" process; their identification poses serious problems because, as said before, the productions often don't present trace elements, inclusions and growth lines and their appearance, iridescence and clarity make them similar to the natural Alexandrites of the Brazilian Hematita deposit.

Theoretically, today's technology would make the replica of a synthetic Alexandrite possible, with a trace composition similar to natural: no certain evidence is there, but technically this can be made.

So, in addition to microscope, sophisticated instruments are necessary such as the FTIR and other spectrophotometry, the mass spectrometer; laser probe, but above all skill and experienced gemologists. In short, this is no easy job.

Not just a gem

Being consumers' perception affected by its rarity and high cost natural Alexandrite in jewelry does not have a great diffusion and visibility, like many other colored stones other than the "triad" Emerald, Ruby and Sapphire. Traders are not keen to proposing, buying or displaying it, and so nobody knows it or asks for it, the jeweler does not buy it... the classic and typical circuit making a product "invisible" in the trade.

By paradox the synthetic Alexandrite is more common than the natural one, due to its wide availability in an extended range of sizes and cutting styles. Since the natural one is quite difficult to find, the synthetic one appropriates the exclusive and magic property of the change of color, which, together with the reputation of its name, makes it desirable.

As for the main consuming markets, in addition to Italy, the U.S., China and India must be mentioned. But its use as a gem, as we have seen, is not the only one for this extraordinary lab created material: synthetic Alexandrite for industrial use - mainly for laser rods - has a growing and strong demand (the price varies depending on the size and dopant composition).



Fig. 44-45 Cut Alexandrites, under artificial and natural light corresponding to the two types of production. Left, four darker pieces and right side, five lighter ones. (Photo:Alberto Malossi)

At this point, it is worthwhile to take a look at its laser properties that can be defined as unique:

- it is highly anisotropic with a low symmetry orthorhombic crystal structure and consequently the absorption and gain properties depend on the difference of the polarization of the light;
- it has a extended emission bandwidth, therefore “tunable” (the wavelength can be modulated basing on uses);
- it tolerates high temperatures and therefore high pulse energies.

These characteristics make Alexandrite, among the crystals at the solid state, the most suitable for a wide range of medical applications, mainly in the dermatological field, because its wavelength is within the absorption spectrum of melanin, allowing treatments of aesthetic dermatology such as removal of tattoos (growing sector), removal of dermal stains, depilation, angiology and dentistry, lending itself to other industrial uses in spectroscopy, optics and meteorology.

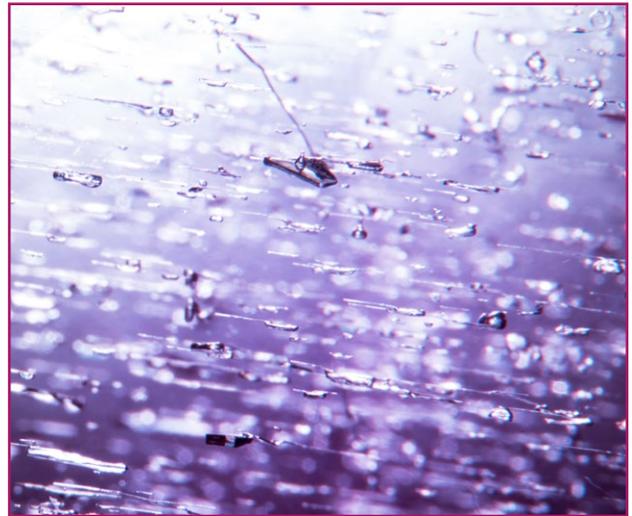


Fig. 46 Crystalline inclusion. (Photo:Alberto Malossi)

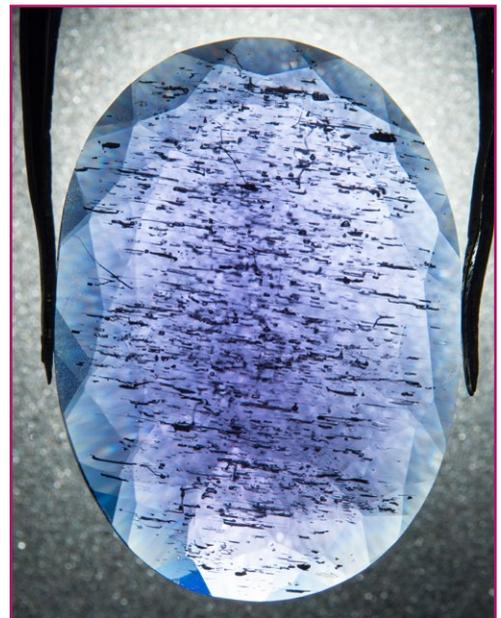
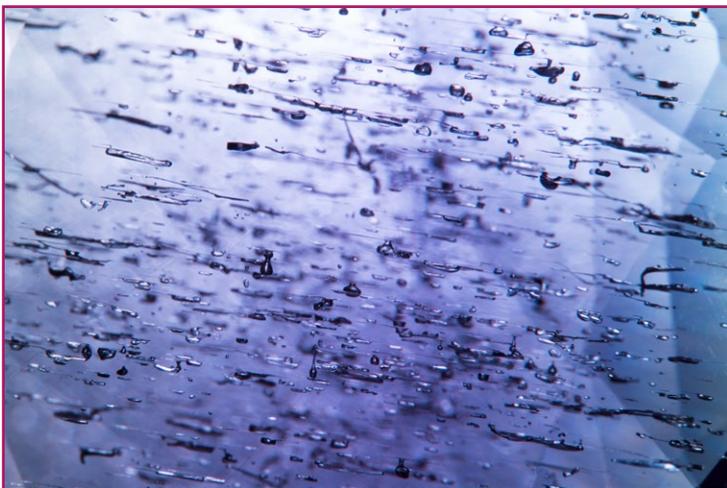


Fig. 47-48 Bubble inclusions oriented according to the growth axis C. (Photo:Alberto Malossi)



Fig. 49 Curved growth lines. (Photo: Alberto Malossi)

Conclusions

Synthetic Alexandrite is one of the most fascinating synthetic materials for its history, its unique characteristics, its importance in the industrial field. But in the gemological field there are no recent studies, perhaps because it is not widespread enough or perhaps because we think we already know everything about it. However, there is much to be said on the matter, as demonstrated by the masterful gemological study of Trossarelli more than thirty years ago, cited in every bibliography on the subject. Does anybody accept the challenge?

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