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The Synthetic Quartz Problem

Fig. 1. A suite of faceted synthetic amethyst, citrine and smoky quartz (far right), of 6.84 cts. to 57.83 cts.

Synthetic quartz is a huge industry problem, yet it goes mostly unnoticed. Perhaps the feeling is that as an inexpensive gem, it is not worth the bother to detect and disclose. However, in the quantities in which it is sold, millions of dollars are at stake, not to mention that sellers are still legally obligated to properly identify and disclose all synthetic gem materials.

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Trigonal crystallizing SiO_2, better known under the name "quartz," makes up approximately 12% of the earth's crust and is one of its main constituents after the feldspars. Quartz in gem quality is abundant with extensive occurrences around the globe. While natural untreated colorless (rock crystal), brown (smoky) and purple to violet (amethyst) quartz are very common to relatively common, natural untreated yellow to orange quartz (citrine) is rare and the great majority of the material found in the market is produced by heat treating amethyst. In this simple treatment at relatively low temperature (300 - 500°C) the Fe^{4+} color center responsible for the purple to violet coloration is destroyed and precipitates as iron oxides that are responsible for the color of these citrines. Certain amethysts from Montezuma in Minas Gerais/Brazil, Four Peaks/Arizona (USA), the border region of California/Nevada (USA) and Zimbabwe will turn green or greenish yellow upon heat treatment. Green quartz can also be produced

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Fig. 2-Left. Zoning in a synthetic ametrine, field of view 10mm. Right: A necklace made up of faceted beads (diameter 20mm each) of synthetic greenish yellow quartz.

by gamma irradiation. Irradiation can be used to create smokey quartz out of colorless material or to deepen the color of brown quartz by valence modification of the impurities of Al, Na, Li and H (in natural quartz). As an example, during the process, the irradiation energy transforms Al^{3+} to Al^{4+} by removing one electron. Then the released electron is caught by a cation such as Li^{+} which then becomes neutral (Li^{0}), this way creating a brown color center. Even though both natural and treated quartz are relatively inexpensive and the supply of such material would likely be more than sufficient for the demand of the market, the appearance of hydrothermal synthetic quartz in the late 1970s in the gem market had a large impact on the quartz market.

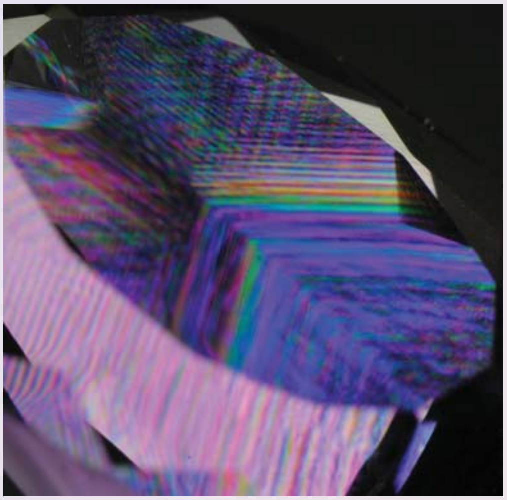
Synthetic quartz crystals grow in an autoclave under pressure and moderate heat on seed crystals, either in a near-neutral NH_4F or much more frequently in an alkaline K_2CO_3 solution (Balitsky et al., 1975; Khadzi et al., 1975). The only commercially interesting varieties of synthetic quartz are citrine, amethyst (Fig. 1), ametrine (Fig. 2, left) and some colors that do not exist in nature (except colored by inclusions) e.g., blue quartz. Some "mishappened" synthetics may resemble smokey quartz (Fig. 1, far right), likely due to irradiation of synthetic quartz with a simultaneous content of Fe^{2+} and Fe^{3+}, but these are rarely seen.

The appearance of hydrothermal synthetic ametrine (bicolored amethyst-citrine quartz) in the 1990s has yet again poured fire into the synthetic quartz problem. Ametrine quartzes are partly colored by Fe^{4+} (Fe^{3+} oxidized to Fe^{4+} by irradiation) (ametrine) and partly by Fe^{3+} (citrine); this quartz variety exists naturally from the Anahí Mine in Santa Cruz, Bolivia, or rarely Brazil, Madagascar and India. The color could most likely be artificially created by irradiation of rare natural color citrine quartz with the part of the stone that should remain citrine protected from the irradiation; it can certainly not be produced by irradiation of "citrine" produced by heating amethyst since such "citrine" has lost real color centers and is colored by precipitated clusters of iron oxides. Theoretically, an ametrine color could be induced by differential heat treatment of amethyst quartz (with one side of the stone cooled), although such material would certainly look different than the natural ametrine and likely much less attractive. Therefore, none of these theoretical treatments make much sense. Finally, this quartz variety can be grown synthetically by the hydrothermal synthesis. To obtain ametrine and not simple amethyst, a sectored distribution of Fe^{2+}/Fe^{3+} during the crystal growth is necessary, so that upon oxidation by irradiation treatment with gamma rays or electrons after the growth, Fe^{3+} (citrine) and Fe^{4+} (amethyst) are created in the corresponding sectors.

A lighter and slightly greenish yellow synthetic quartz that resembles gamma irradiation treated natural quartz is another type of synthetic quartz that has entered the market some time ago and that may be extremely difficult to identify when free of inclusions (Fig. 2, right).

All above information leads to the problems that exist today with synthetic quartz. Much of it is in the market, frequently mixed within parcels of natural quartz. The material is often not easily identified, unless by a qualified and well equipped laboratory. And, there are cases where the identification of natural or synthetic origin is close to impossible. The other big problem is that many are not aware that this problem is so prominent. It is estimated that in certain markets there are more synthetic amethysts than natural stones. Yet another point is the relatively low price of natural quartz. Therefore, sending such low cost gems to a lab for in-depth analysis seems outrageous to many, since the analysis cost may be higher than the value of the stone.

Fortunately, not all synthetic quartzes are difficult to identify but the identification often appears to be detective work looking for as many indications possible to come to a final conclusion. Initially, the identification of synthetic amethyst was easy since no twinned material was synthesized. Therefore, all of the early material could be identified under crossed polarizing filters. Almost all natural amethyst (and in consequence citrine produced by heat



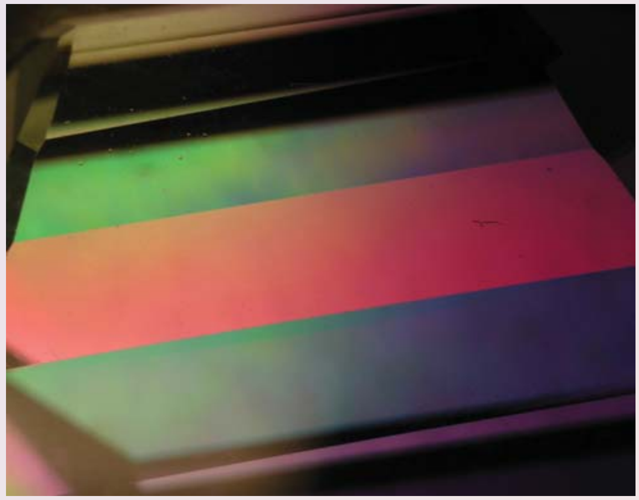


Fig. 3. Left. Brazil twinning seen under crossed polarizing filters in a natural amethyst, field of view 25mm. Right: The appearance of untwinned synthetic amethyst under crossed polarizing filters; field of view 35mm.

treatment of amethyst) show polysynthetic twinning according to the Brazil law, which was never present in the older productions of synthetic quartz (Notari et al. 2001) (Fig. 3). The only exceptions to this rule seem to be the natural amethysts from the Brandberg area in Namibia and many of the amethysts from Mexico that lack Brazil twinning. Note that there are likely small commercially irrelevant sources for amethyst where the stones could exhibit the same property of being untwinned.

Brazil twinning results in spectacular interference patterns (Brewster fringes), observable under crossed polarizing filters analyzing the sample from the top and parallel to the optical axis ("c"), in immersion (Fig. 3, left). These interference fringes are situated in the major rhomboedron ("r") and correspond to polysynthetic twinning. They consist of alternating lamella of right quartz “R” and left quartz “L.” These lamellae produce an optical activity induced by the rotating structure of the crystal – left when the tetrahedron spirals wind to the right and right when they wind to the left.

Things became more complicated when the producers of synthetic quartz started to use seed plates that exhibited Brazil twinning, which then logically was also present in the synthetic stones. Luckily this was, and still is, relatively rarely the case and even today the absence of Brazil law twinning in an amethyst or citrine is a good indication that a stone may be of synthetic origin and that it needs further analytical examination. Additionally, some synthetic material may exhibit unusual interference and extinction patterns under crossed polarizing filters. Under crossed polarizing filters in some synthetic quartz, triangular gray strain patterns (Dauphiné twinning) within the interference colors seen along the c axis and situated in the minor rhomboedron (“z”) can be seen. These can only rarely be seen in natural quartz but are not uncommon in synthetic quartz (Fig. 4).

Besides the Brazil twinning and features under polarized light, it is a good thing that by far, most faceted quartz - natural and synthetic - has at least some tiny inclusions that can be spotted by a high power microscope. Fortunately, the inclusions in synthetic and natural quartz look quite different. The most characteristic inclusions in all types of synthetic quartz are the so-called “breadcrumb” inclusions. The name says it all. These small to tiny usually brownish particles look very much like little crumbs of bread (Fig. 5, left). They are either randomly scattered or, if the seed still is present, additionally distributed on two planes along the seed plate (Fig. 5, right). These particles represent remnants of the seed material used to grow such quartz in the hydrothermal autoclaves. In some natural quartz there can be particles that somewhat resemble the breadcrumbs, but one can generally distinguish them based on their appearance. The particles in natural quartz look more like tiny white cotton flakes.

Natural quartz typically contains multiphase inclusions (liquid, gaseous and solid) (Fig. 6, left) characteristic for hydrothermally formed minerals and rare in syn-

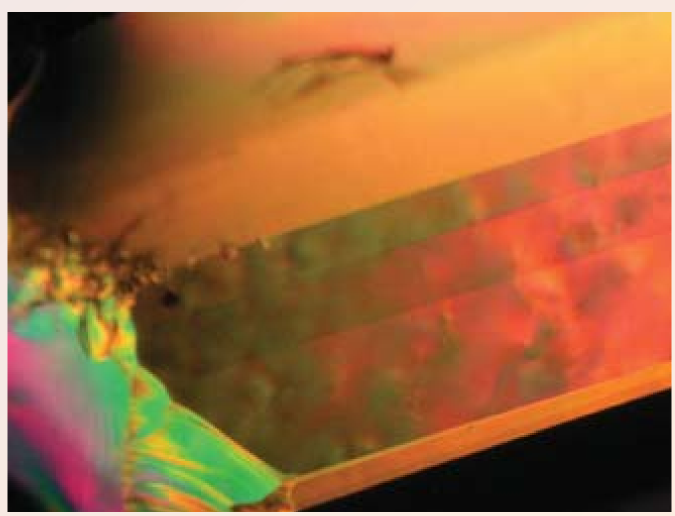
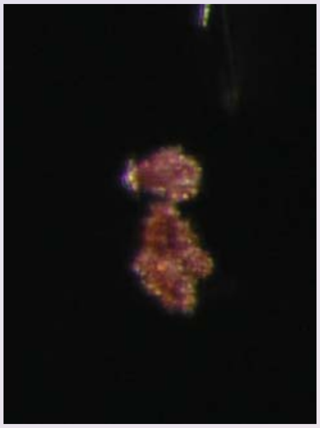


Fig. 4. An untwinned synthetic amethyst exhibiting triangular gray strain patterns within the interference colors under crossed polarizing filters; field of view 30mm.



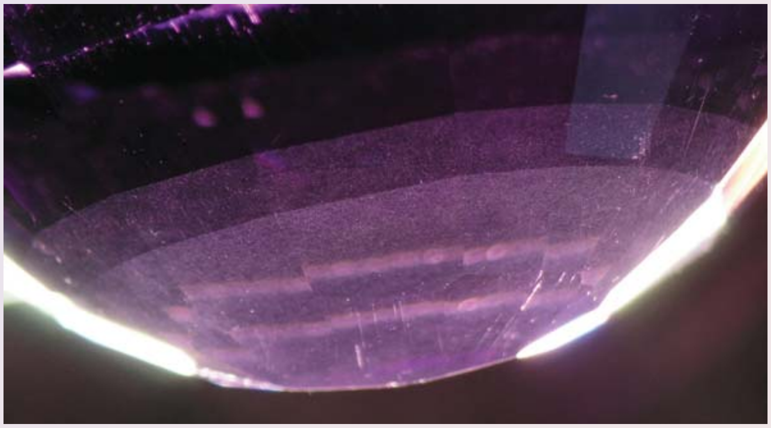


Fig. 5. Left. A "breadcrumb" inclusion in a synthetic amethyst. The beige to brown color of that inclusion and the granular appearance are typical for these particles seen in synthetic quartz. Field of view approx. 0.75mm. Right: A synthetic amethyst with seed crystal, along which tiny "breadcrumb" inclusions are aligned; field of view 30mm.

thetic quartz; if two-phase inclusions (liquid, gaseous) are present in synthetic quartz, then they are generally elongated and only extremely rarely distributed within veils such as is the case in most natural amethyst and consequently citrine. One type of multiphase inclusion characteristic for synthetic quartz is the so-called "nail-head spicule," liquid filled growth channels terminated by an inclusion on one side (Fig. 6, center and right).

The nail-head spicules are characteristic inclusions in synthetic beryl and quartz and similar inclusions have been described in some natural gemstones (Choudhary and Golecha, 2007). Therefore, the occurrence of isolated inclusions of this type is not proof of synthetic origin. Nevertheless, the appearance of nail-head spicules in quartz is generally typical for synthetic material, since the "heads" of these inclusions consist of the most characteristic and common inclusion in synthetic quartz—the breadcrumb inclusions described above. Nail-head spicules are always oriented parallel to the c-axis. Sometimes, such inclusions are very large or simply brought to the surface, and then they will appear like hollow funnel-shaped channels. Only in some of the large cavities, the breadcrumb inclusions can be found at the narrow side of the channel. All these features are attributed to fast growth of the synthetic quartz crystals.

Synthetic amethyst practically never shows the typical strong color zoning sometimes present in some natural amethyst, with angles following the prism ("m") and the pyramidal faces ("r", "z"). The synthetic material exhibits extremely sharp color zoning in the cases when the seed crystal was not removed from the cut stone. The seed is commonly colorless while the rest of the stone is purple to violet (Fig. 7, left). In ametrines, immersion techniques can often reveal very unusual flame-like color zones (Fig. 7, center) and different orientations between the citrine and the amethyst sectors. The citrine bands follow the "c" plane (the zones are thus perpendicular to the "c" axis) while the amethyst zoning follows the "r" (rhombohedral) sector. In natural ametrine, the amethyst color is confined to the "r" (rhombohedral) sector which can occupy the entire volume of the crystal's pyramidal extremity, while the citrine follows the "z" (rhombohedral) sector. In some synthetic quartz, especially synthetic citrines, the color distribution can be

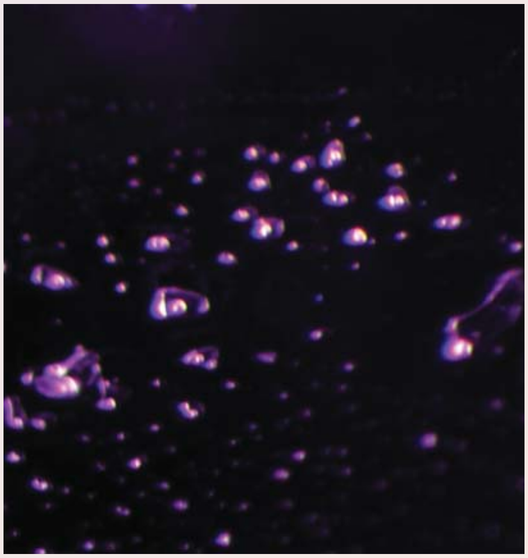


Fig. 6. Left. Two-phase inclusions in a veil in a natural amethyst from Siberia; field of view 2mm. Center and right: Multi-phase inclusions in synthetic citrine, so called "nail-head spicules"; field of view 0.75mm (center), 8mm (right).

Fig. 7. Left. Color zoning due to a colorless seed crystal in a synthetic amethyst; field of view 15mm. Center: Flame-like color zones in a synthetic ametrine; field of view 5mm. Right: Streaky color zoning in a synthetic citrine; field of view 20mm.

most unusual, being streaky (Fig. 7, right) and appearing like straight striae in some samples.

Spectroscopic methods only have led to limited success in the task to distinguish all synthetic and natural quartz. Synthetic amethysts grown in NH_4F solution are relatively easy to identify by infrared spectroscopy, since they usually exhibit characteristic infrared absorption bands at 3630, 3664 and 3684 cm^{-1} (Balitsky et al., 2004). In synthetic amethyst grown in a K_2CO_3 solution, this method is less reliable. In earlier publications, the 3543 cm^{-1} infrared absorption was indicated as proof of synthetic origin but it was soon found that this peak can also be found in natural amethysts. Only recently, an absorption feature really indicative for synthetic amethysts was published by Karampelas et al. (2005). The 3595 cm^{-1} peak is a rare feature in synthetic amethyst and if present, then it is much larger (FWHM) than in natural amethyst, where it occurs much more frequently (depending of the deposit). To properly determine the widths of this band, spectra need to be recorded at high resolution. Unfortunately, this peak is not present in all natural amethyst either, thus this test alone cannot always be used to distinguish such material. Another indication of synthetic origin is unusually intense water FTIR absorption. Frequently, the water content of synthetic quartz appears high compared to natural quartz. The author found that synthetic citrines frequently exhibit infrared spectra with very intense water absorption (centered at about 3200 cm^{-1}), which is uncommon in natural citrine. Conclusively it can be stated that synthetic quartz is, and will remain, a serious problem in the gem market. It is crucial to buy quartz only from the most reliable sources possible. Buying amethyst, ametrine and citrine in the free market based only on the lowest price is risky since the chance is exceedingly high that at least some of the material would be synthetic. The fact that 70% of faceted quartz that was sent to the GEMLAB laboratory in 2008 was of synthetic origin is a very evident example of the quantities of synthetic quartz in the market. While the identification of origin of quartz (natural versus synthetic) can be very difficult or even impossible, detailed microscopic observations using high magnification, immersion and crossed polarizing filters can in many cases be sufficient to distinguish synthetic from natural quartz. ◆

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