AN UPDATE IN THE SEPARATION OF NATURAL FROM SYNTHETIC AMETHYSTS

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Abstract

Since the first synthetic amethyst was commercially manufactured about 30 years ago, the separation from natural material has been difficult for gemologists. Even today, the separation of natural from hydrothermally grown in K_2CO_3 synthetic amethyst is still an issue. With only the help of classical gemological criteria (such as inclusions, twinning and color zoning) it is difficult to separate synthetic stones from their natural counterparts. The separation problem is even more complex in the case of the highest quality (and value) of amethysts presenting neither inclusion nor twinning nor color zoning. IR absorption spectra of amethyst in the region of the X-OH group stretching (particularly from 3000 to 3900 cm^{-1}) reveal several bands that have been used for the separation of natural from synthetic amethyst. Using a resolution at 0.5 cm^{-1} the 3595 cm^{-1} band is present in all natural amethyst and in some rare synthetic ones. When present in synthetic amethysts, its full width at half maximum (FWHM) is about 7 cm^{-1}, whereas it is about 3.3 cm^{-1} in all naturals. This new criterion worked for all of our samples.
Key words: *gems, infrared spectroscopy, FWHM.*

Περίληψη

Ο διαχωρισμός συνθετικών και φυσικών αμέθυστων προβληματίζει τους γεμμολόγους από τότε που εμφανίστηκαν οι πρώτοι συνθετικοί κρύσταλλοι αμέθυστου στην αγορά, περίπου 30 χρόνια πριν. Το πρόβλημα του διαχωρισμού παραμένει μέχρι και σήμερα, όσο αναφορά κυρίως στο διαχωρισμό των φυσικών αμέθυστων από αυτούς όπου έχουν συντεθεί υδροθερμικά σε διάλυμα K_2CO_3. Χρησιμοποιώντας αποκλειστικά τα κλασσικά γεμμολογικά κριτήρια (τα οποία περιλαμβάνουν τη μελέτη εγκλεισμάτων, διδυμιών και ζωνών χρώματος), ο διαχωρισμός δε καθίσταται πάντα εφικτός. Το πρόβλημα είναι πιο έντονο όσο αναφορά στους υψηλής ποιότητας (άρα και αξίας) κρυστάλλους, όπου δε παρουσιάζουν ούτε εγκλείσματα, ούτε διδυμίες ούτε ζώνες

χρώματος. Επίσης, κάποιες χαρακτηριστικές απορροφήσεις σε φάσματα υπερύθρου αμέθυστων, ιδιαίτερα στη περιοχή 3000 έως 3900 cm⁻¹ όπου παρατηρείται η δόνηση των μορίων υδροξυλίου (X-OH), χρησιμοποιήθηκαν για το διαχωρισμό φυσικών και συνθετικών αμέθυστων. Για τη παρούσα εργασία έγιναν μετρήσεις απορρόφησης υπερύθρου φωτός των φυσικών αμέθυστων, υπό υψηλή διακριτική ικανότητα (0.5 cm⁻¹), σε φυσικούς και συνθετικούς λίθους. Παρατηρείται ότι η απορρόφηση στα 3595 cm⁻¹ είναι παρούσα σε όλα τα φυσικά δείγματα (με εύρος στη μέση του ύψους - Full Width Half Maximum- περίπου 3.3 cm⁻¹) ενώ απουσιάζει από τα συνθετικά δείγματα (στη μοναδική περίπτωση όπου είναι παρούσα έχει FWHM: 7 cm⁻¹). Το παραπάνω κριτήριο ισχύει σε όλα τα δείγματα όπου εξετάστηκαν μέχρι σήμερα.
Λέξεις κλειδιά: *πολύτιμοι λίθοι, φασματοσκοπία υπερύθρου, FWHM.*

1. Introduction

Amethyst exceptional color draws the attention of gemologists, mineralogists and general public alike. Because of this it is an important material of the jewelry industry. Today's major problem is the presence of significant quantities of synthetic amethyst on the market. These amethysts should cost less than their natural counterparts. With only the help of classical gemological techniques (such as the study of inclusions, twinning and color zoning) it is difficult to separate synthetic stones from their natural counterparts (Fritsch *et al.* 1987a, Fritsch *et al.* 1988a, Fritsch *et al.* 1995, Notari *et al.* 2001). The separation issue is compounded even more in the case of the highest quality (and value) of amethysts, which typically presents neither inclusion nor twinning or color zoning. The impact of this is a lack of confidence from the buyers and has prompted much research into identifying the synthetic material with certainty. In particular, arguments based on the presence or the absence of certain infrared absorption bands proved promising (Fritsch *et al.* 1987a, Fritsch *et al.* 1988a, Fritsch *et al.* 1995, Notari *et al.* 2001, Smaali, 1998, Zecchini *et al.* 1999, Karampelas *et al.* 2005). The most recent argument (Karampelas *et al.* 2005) is tested in this paper on a large number of samples.

2. Background

2.1. Natural amethyst

Quartz has many colored varieties. The most common varieties, which are used as gems are: colorless quartz (rock crystal), violet-purple (amethyst), yellow (citrine), pink quartz and green quartz (prasiolite). Amethyst color is caused by $O^{2-} \rightarrow Fe^{4+}$ charge transfer, the rarer 4^+ valence of iron being due to irradiation (Fritsch *et al.* 1988b). Their point group is 32 and their space group is P 3_1 2, P 3_2 2. The most intense color is concentrated in the major rhombohedron and occasionally in the minor rhombohedron (Balitsky, 1981). Like other varieties of quartz, amethysts can be found in various geological environments. They occur in geodes of basaltic rocks e.g. Brazil (Rio Grande do Sul), Uruguay (Artigo) etc. Amethyst crystals can also be found in pegmatite e.g. in Mexico (Vera Cruz), Madagascar etc. In some rare cases they form in alluvial deposits, as in Minas Gerais in Brazil. Countries with the most important gem quality production of amethysts used in jewelry, are presented in Table 1 (Webster 1975).

2.2. Synthetic amethysts

With the growing interest on synthetic amethyst, scientist tried to synthesize crystals of higher quality, without cracks etc. The hydrothermal method is issued exclusively either in a near neutral NH_4F or in an alkaline K_2CO_3 solution (Balitsky *et al.* 1975, Khadzi *et al.* 1975). The vast majority of synthetic amethysts present on the market today is grown in K_2CO_3 solutions (Fritsch *et al.* 1995, Balitsky 2004b).

Table 1 - Countries or states with the most important production of gem-quality amethysts

Continent	Country or State
Africa	South Africa, Madagascar, Namibia, Zambia, Zimbabwe
North America	Arizona, Canada, Colorado, Maine, New Jersey
South America	Brazil, Bolivia, Mexico, Uruguay
Asia	China, India, Japan, Korea
Europe	Russia
Oceania	Australia

2.3. Separation of natural from synthetic amethysts

The first synthetic amethyst crystals were commercially synthesized since 1975 (Bariand *et al.* 1998). Gemologists used classical gemology (twinning, inclusions and color zoning) as well as laboratory methods (FTIR) to identify this material.

2.3.1. Classical gemology

2.3.1.1. Twinning

To use this test, only a polariscope and an immersion cell are needed. The test popularized by Schmetzer in 1985, relies on the fact that natural amethysts are polysynthetically (Brazil law) twinned, whereas synthetic amethysts grown are not (Crowningshield *et al.* 1986, Fritsch *et al.* 1987a, Fritsch *et al.* 1988). If twinning is observed when looking down an amethyst's optic axis under crossed polarizers, that gem can be identified as natural. Only synthetic amethysts grown in NH_4F never present twinning. Synthetic amethysts grown in K_2CO_3 may present twinning; it appears in an irregular (flame-like twin pattern) form (Crowningshield *et al.* 1986, Fritsch *et al.* 1989, Notari *et al.* 2001). By contrast, natural amethysts twinning forms a characteristic angle of 60° or 120° (Crowningshield *et al.* 1986). However, natural amethysts (from Altiplano, Bolivia) were found with twinning of different angles (Notari *et al.* 2001). Fritsch and Koivula (1989) show that twinning in synthetic amethyst sometimes cannot be separated from that present in the natural. Additionally, natural amethysts that do not present twinning were found (Crowningshield *et al.* 1986, Fritsch *et al.* 1987a, Fritsch *et al.* 1988, Notari *et al.* 2001). Thus, it is obvious that this method is not always effective.

2.3.1.2. Inclusions

Another classical gemological method useful for the separation is the examination of inclusions. For this method the microscopic study is sufficient. Natural amethysts can contain the inclusions cited below (Gübelin *et al.* 1986, Fritsch *et al.* 1987a, Fritsch *et al.* 1988):

- blood-red plates of lepidococite,
- brooms or needles of goethite,
- circular concretions of orange limonite and black hematite,
- negative crystals with fluids inclusions,
- comet-like stringers of numerous tiny two-phase inclusions.

Typical inclusions in synthetic amethysts are:

- synthetic eucryptite "breadcrumbs",

- spike-shaped two-phase (liquid and gas) inclusions, because of the hydrothermal origin (not always synthetic).

Synthetic eucryptite can be found in some rare natural stones (Crowningshield *et al.* 1986). When inclusions are present, they are a very good way to separate natural from synthetic amethysts, but it is not generally the case of high value amethysts, which often contain no inclusions.

2.3.1.3. Color zoning

Color zoning is seen using a microscope, with diffused transmitted light. When color zoning is seen in a synthetic amethyst, it is limited to darker and lighter shades of purple. The color zoning in natural amethysts is typically straight or angular in two or three directions and might consist of purple and violetish blue zones, sometimes contrasting with near-colorless zones (Crowningshield *et al.* 1986). A near-coloress zone has not been reported in a synthetic amethyst (Fritsch *et al.* 1987a, Fritsch *et al.* 1988). Wavy color zoning is a common feature of synthetic amethysts and is rarely seen in natural stones. Although color zoning alone is not enough to ascertain the origin of a stone, study of zones is a useful auxiliary test.

2.3.2. Laboratory method (FTIR)

Infrared spectroscopy is a powerful tool for gem identification and research. Absorption peaks of a gem material in the infrared region of the electromagnetic spectrum are due to vibrations of molecules in the crystal structure. They can be used to separate one gem from another or natural from synthetics gems or to detect some treatments (Fritsch *et al.* 1987b).

Infrared absorption in the region of X-OH group stretching mode (particularly from 3000 to 3900 cm^{-1}) has been suggested as a useful method to separate synthetic from natural amethysts (Zecchini 1979, Fritsch *et al.* 1987a, Fritsch *et al.*1988, Fritsch *et al.* 1995, Smaali 1998, Zecchini *et al.* 1999, Notari *et al.* 2001, Balitsky *et al.* 2004 a, b). The identification of crystals grown in NH_4F solution is easy through the observation of their specific infrared absorption bands at 3630, 3664 and 3684 cm^{-1} (Balitsky *et al.* 2004 a, b). In the case of crystals grown in K_2CO_3 (referred to as simply "synthetic amethyst" thereafter) separation is more difficult (Zecchini 1979, Fritsch *et al.* 1987, Fritsch *et al.*1988, Fritsch *et al.* 1995, Smaali 1998, Zecchini *et al.* 1999, Notari *et al.* 2001, Karampelas 2002, Karampelas *et al.* 2004, Balitsky *et al.* 2004 a, b). Generally, synthetic and natural amethysts have almost the same spectrum in this region. Both of them present two absorption peaks at 3585 and 3612 cm^{-1}, due to the presence of OH- in the quartz structure (Kats 1962). A band at 3543 cm^{-1} occurs rarely in natural amethysts but is observed in the overwhelming majority of synthetic ones. Furthermore, it has been proposed that the 3595 cm^{-1} absorption peak is present in natural amethyst only (Zecchini 1979, Smaali 1998, Zecchini *et al.* 1999).

Balitsky and colleagues (2004 a, b) have demonstrated that the 3543 cm^{-1} band is not as rare in natural amethysts as commonly believed and it may be absent in some synthetic amethysts. In addition, they have demonstrated that this band reflects certain crystal growth conditions common in both natural and synthetic amethyst. Namely, this peak is indirectly related to the negative rhombohedron growth sector. This sector dominates in most commercial synthetic amethyst, but is minor to absent in natural amethyst crystals. Therefore, the absorption band is much less common in natural amethyst but is present in the majority of the synthetic samples because of their different growth conditions, thus it cannot be considered a characteristic absorption feature of synthetic amethyst. Moreover, the 3595 cm^{-1} band may be present in some synthetic amethysts (Karampelas 2002, Karampelas *et al.* 2004, Karampelas *et al.*arampelas et al. 2005) and absent from some natural ones (Kitawaki*et al.* 2004 a, b). Measurements on selected samples (these samples were selected because they violated the separation criteria previously proposed), using (non-standard) high resolution of 0.5 cm^{-1}, have shown that separation can be performed based on the presence and full width at half maximum (FWHM) of the 3595 cm^{-1} band (Karampelas *et al.* 2005). More precisely, at that resolution, the 3595 cm^{-1} band has its true shape and it was documented in natural amethysts and rarely in the synthetics. If this band is present in synthetic amethysts its FWHM is

7 cm^{-1} approximately twice that measured in natural amethysts (about 3 cm^{-1}) (Karampelas *et al.* 2005).

As observed by previous authors (Smaali 1998, Zecchini *et al.* 1999), there is no direct correlation between the intensity of the color and the infrared absorbance in the region of X-OH group stretching (which apparently depends mostly on water content). In most cases, the orientation of the beam relative to the crystallographic axes, typically does not induce a very significant change in intensity (Smaali 1998, Zecchini *et al.* 1999, Balitsky *et al.* 2004b, Karampelas 2002, Karampelas *et al.* 2005). So the relevant peaks can be detected in spectra taken in random orientations, which is useful for the identification of faceted gems, for which crystallographic orientation is typically unknown, and sometimes hard to ascertain.

3. Materials and Methods

The current study is based on the measurement of the intensity and shape, of bands useful for amethyst separation, on 30 natural (Table 2) and 10 synthetic (Table 3) amethysts at resolutions of 4 and 0.5 cm^{-1}. Measurements on crystallographically oriented crystals (cut parallel and perpendicular to c-axis) were obtained on a Bruker 113v FTIR spectrometer, in vacuum, at the Physics Department of Aristotle University of Thessaloniki, Greece. Measurements on faceted stones, took place on a FTIR Bruker Vertex 70 at the IMN (Institut des Matériaux Jean Rouxel, France) using a diffuse reflectance accessory as a beam condenser. To obtain a good signal to noise ratio, in many cases long measurements were necessary (see "scans" in Tables 1 and 2; a measurement of 1024 scans at 0.5 cm^{-1} resolution takes about 1h and 30 min.). The full width at half maximum (FWHM) of the 3595 cm^{-1} band is measured by a classic method: a linear background passing through the bottom of the transmission windows on either side of the peak is subtracted, the half-height is determined relative to this linear background, and the half-width is measured at half height parallel to the linear background.

4. Results

Infrared absorption spectra in the range 3500-3640 cm^{-1} of various test amethysts are presented in figures 1 to 5. The spectra corresponding to the two different resolutions are stacked, and offset in absorbance for clarity. In all figures, the upper spectra are taken at a resolution of 0.5 cm^{-1}, and the lower ones with a 4 cm^{-1} resolution. The intensities of the peaks vary from one stone to another, but are unaffected by color intensity.

4.1. Natural amethysts

Table 1 presents the natural amethysts tested:

- The 3585 and 3614 cm^{-1} bands are present in all samples (e.g. Figs from 1 to 3).

- The 3543 cm^{-1} absorption band is weak but distinct in some of the samples (e.g. Fig. 1).

- The 3595 cm^{-1} absorption band, although clearly seen in majority of our samples at 4 cm^{-1} resolution (e.g. Fig. 2), is hard to make out in some cases (Figs 1 and 3). At 0.5 cm^{-1} resolution, this absorption band is well resolved in all of our natural samples (Figs 1-3).

The full width at half maximum (FWHM) of the 3595 cm^{-1} absorption band for all of our natural samples is about 3.3 cm^{-1} (±0.6 cm^{-1}) (see Figs 1 to 3 and Table 2).

Table 2 - Samples of natural amethysts from different countries, with their weight (or dimension for the oriented crystals), the FWHM of the 3595 cm^{-1} absorption band and the number of scans. Samples with unknown origin "prove" their natural nature under the microscope (inclusions, twinning etc.). Results for the samples with stars have been already published (Karampelas _et al._ 2005)

Country or State of origin/Type	Weight (ct.) or dimensions (mm)	FWHM (cm^{-1}) of 3595 cm^{-1} band	Scans at 4/0.5 cm^{-1} resolution
Bolivia (Altiplano)/oriented	6.5x3.8	3	64/128
France (St. Raphael)/oriented	3.5x3.2	3	64/128
Arizona (Four peaks)/oriented	4.4x3.8	3	64/128
* Bolivia (Anahi mine)/oriented	5.1x4.5	3	64/128
* Mexico (Vera Cruz)/oriented	6.1x5.1	3	64/128
* Namibia (Platveld)/oriented	15.8x9.8	3	64/128
* Madagascar/ oriented	3.2x2.3	3	64/256
Arizona (Four peaks)/faceted	3.4	3	128/1024
Bolivia (Anahi mine)/faceted	4.1	3.2	128/1024
Zambia (Solwezi)/faceted	3.75	3.5	128/1024
Unknown/faceted	4.45	2.9	128/1024
Unknown/faceted	3.6	3.2	256/1024
Unknown/faceted	2.85	3.9	256/1024
Unknown/faceted	1.4	3.3	256/1024
Unknown/faceted	1.1	3.3	256/1024
Unknown/faceted	1.9	3.4	128/1024
Unknown/faceted	1.3	3.2	128/1024
Unknown/faceted	1.85	3.9	128/1024
Unknown/faceted	3.45	3.2	128/1024
Unknown/faceted	2.35	3.3	128/1024
Unknown/faceted	1.35	3.2	128/512
Unknown/faceted	2.6	3.4	128/1024
Unknown/faceted	1.25	3.2	128/1024
Unknown/faceted	1.6	3.9	128/1024
Unknown/faceted	2.25	3.2	128/1024
Unknown/faceted	0.45	2.7	128/1024
Unknown/faceted	1.15	3.7	128/512
Unknown/faceted	2	3.7	128/512
Unknown/faceted	2.55	3.7	128/512
Unknown/faceted	3.05	3.2	256/1024
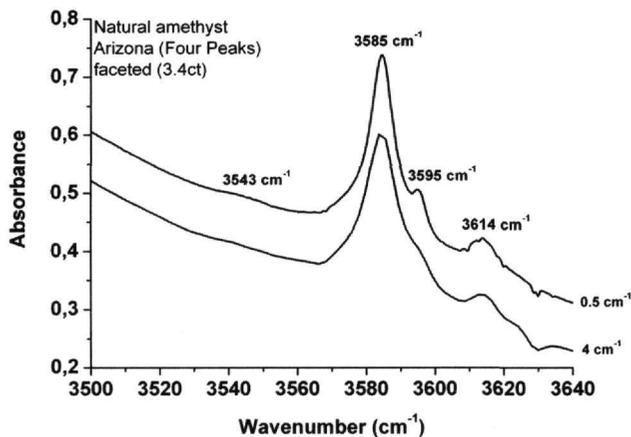
Figure 1 - IR absorption with resolutions of 4 cm⁻¹ (lower spectrum) and 0.5 cm⁻¹ (upper spectrum) for a randomly oriented faceted natural amethyst (3.4 ct.) from Arizona (Four Peaks). The 3595 cm⁻¹ band is difficult to de detected in spectra acquired at 4 cm⁻¹, whereas it is well distinguished at 0.5 cm⁻¹ resolution (FWHM: 3 cm⁻¹). The band at 3543 cm⁻¹ is also observed
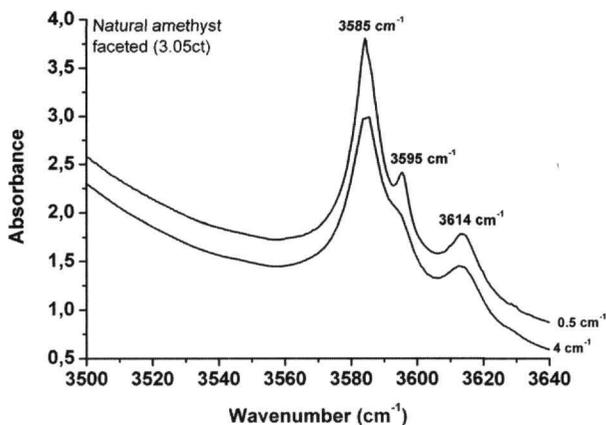
Figure 2 - IR absorption with resolutions of 4 cm⁻¹ (lower spectrum) and 0.5 cm⁻¹ (upper spectrum) for a randomly oriented faceted natural amethyst (3.05 ct.). The 3595 cm⁻¹ band is more difficult to be detected in spectra acquired at 4 cm⁻¹ than at 0.5 cm⁻¹ resolution (FWHM: 3.2 cm⁻¹)

4.2. Synthetic amethysts

Table 3 presents the synthetic amethysts tested:

- The absorption peaks at 3543, 3585 and 3614 cm⁻¹ bands are present in all samples (e.g. Figs 4 and 5).

- The 3595 cm⁻¹ absorption band is detected in only one of the synthetic samples. The FWHM of this peak at a resolution of 0.5 cm⁻¹ is about 7 cm⁻¹ (±1 cm⁻¹) (Table 3).
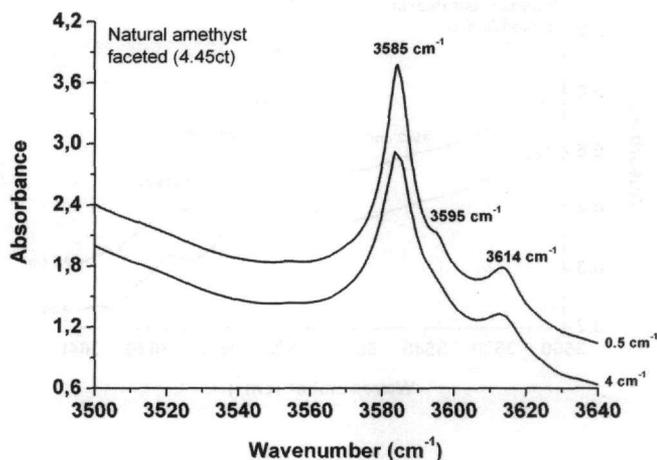
Figure 3 - IR absorption with resolutions of 4 cm⁻¹ (lower spectrum) and 0.5 cm⁻¹ (upper spectrum) for a randomly oriented faceted natural amethyst (4.45 ct.). The 3595 cm⁻¹ band is barely seen in spectra acquired at 4 cm⁻¹, whereas it is well discriminated at 0.5 cm⁻¹ resolution (FWHM: 2.9 cm⁻¹)

Table 3 - Samples of synthetic amethysts grown in a K_2CO_3 solution from different countries with their weight (or dimensions for the oriented crystals), the FWHM of the 3595 cm⁻¹ absorption band (if it exists) and the number of scans. Results for the samples with the stars have been already published (Karampelas *et al.* 2005)

Country or State of origin/Type	Weight (ct.) or dimensions (mm)	FWHM (cm⁻¹) of 3595 cm⁻¹ band	Scans at 4/0.5 cm⁻¹ resolution
*Russia/oriented	3.4x2	7	64/128
*Russia/oriented	4.5x2.9	-	64/512
Russia/faceted	20	-	128/1024
Russia/faceted	29.25	-	128/1024
Russia/faceted	8.45	-	128/1024
Russia/faceted	8.85	-	128/1024
U.S.A. -Sawyer-/faceted	0.65	-	128/512
U.S.A. -Sawyer-/faceted	0.6	-	128/256
U.S.A. -Sawyer-/faceted	0.55	-	128/256
Unknown/ faceted	1.55	-	512/1024
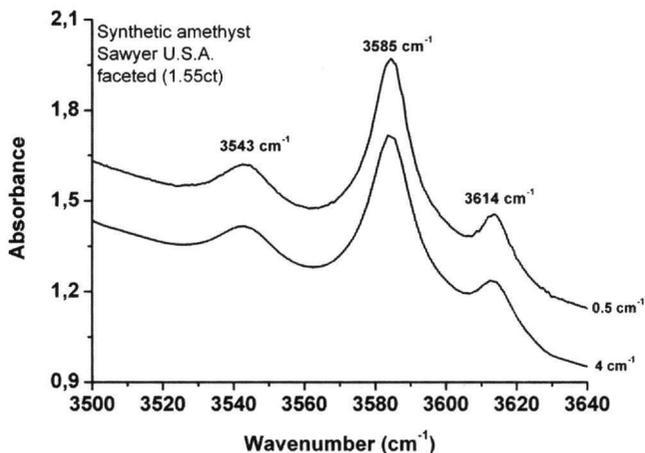
Figure 4 - IR absorption with resolutions of 4 cm⁻¹ (lower spectrum) and 0.5 cm⁻¹ (upper spectrum) for a randomly oriented faceted synthetic amethyst (1.55 ct.) from U.S.A. (Sawyer) grown in a K₂CO₃ solution. No band at 3595 cm⁻¹ is observed. The band at 3543 cm⁻¹ is well developed
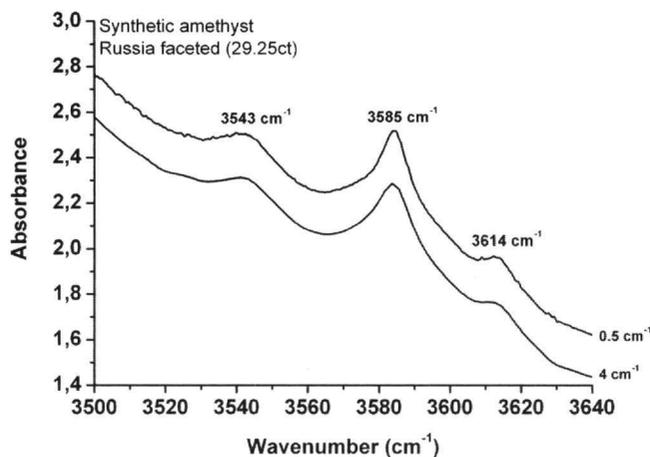
Figure 5 - IR absorption with resolutions of 4 cm⁻¹ (lower spectrum) and 0.5 cm⁻¹ (upper spectrum) for a randomly oriented faceted synthetic amethyst (29.25 ct.) from Russia grown in a K₂CO₃ solution. No band at 3595 cm⁻¹ is observed. The band at 3543 cm⁻¹ is well discriminated

5. Discussion and conclusion

The 3595 cm⁻¹ absorption band is of the greatest interest. It reaches its true shape only at 0.5 cm⁻¹ resolution. Therefore using a resolution of 4 cm⁻¹ (as most laboratories), this band may be missed (e.g. Figs 1 and 3). Previous publications (Kitawaki 2002, Balitsky *et al.* 2004b) state that the 3595 cm⁻¹ absorption band is absent in some natural amethysts. This could be due to inadequate resolution of the spectra. The resolution is 4 cm⁻¹ in the case of Kitawaki's study, but is not mentioned in Balitsky's article. Therefore a resolution of 0.5 cm⁻¹ seems necessary for the

detection of the 3595 cm^{-1} peak. With such a resolution, this peak is detected in all our natural amethysts, with a FWHM of about 3.3 cm^{-1} (±0.6 cm^{-1}).

The 3595 cm^{-1} absorption band is observed in one synthetic sample (Karampelas 2002, Karampelas *et al.* 2004, Karampelas *et al.* 2005). However its FWHM, at a resolution of 0.5 cm^{-1}, is about 7 cm^{-1} (±1 cm^{-1}) (Karampelas *et al.* 2005).

If amethysts of unknown origin received in a gemological laboratory, it is suggested, first of all, to observe them under a microscope. If it is not possible to identify their natural or synthetic origin using classical gemology, an infrared spectrum should be obtained at 0.5 cm^{-1} resolution, with a good signal to noise ratio. If the 3595 cm^{-1} band is absent, then the amethyst is synthetic. If the 3595 cm^{-1} band is present with a FWHM of about 7cm^{-1} (±1 cm^{-1}) the amethyst is also synthetic. It is otherwise natural (3595 cm^{-1} band with FWHM of 3.3 cm^{-1} ±0.6 cm^{-1}).

Further research is necessary in order to explore the cause for this small difference in the infrared absorption spectrum of natural and synthetic amethysts. Previous studies (Zecchini *et al.* 1999) have linked the 3595 cm^{-1} band to the presence of boron. A systematic search for this difficult-to-detect impurity in amethyst, using near non-destructive chemical analysis (e.g. Laser Ablation Inductively Coupled Plasma Mass Spectrometry -LA-ICPMS- or Laser Induced Breakdown Spectroscopy -LIBS-) might shade light on the observed differences that have been noticed.

6. Acknowledgments

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