Distinguishing natural from synthetic amethyst: the presence and shape of the $3595\,cm^{-1}$ peak

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Summary

The infrared absorption spectrum of amethyst in the region of stretching vibrations of X–OH groups reveals several bands that have been used for the separation of natural from synthetic amethyst. The intensity and shape of these bands have been measured as a function of crystallographic orientation. Using a resolution of $0.5\,cm^{-1}$ the $3595\,cm^{-1}$ band is present in all infrared spectra of natural amethyst and in some rare synthetic ones. If present in synthetic amethyst, its full width at half maximum (FWHM) is about $7\,cm^{-1}$, whereas it is about $3\,cm^{-1}$ in all natural samples. This new criterion, unlike the previous ones, seems appropriate to separate natural from synthetic amethyst in all cases.

Introduction

Amethyst is an important material for the jewelry industry. Since the first amethysts were commercially synthesized about 30 years ago, their identification has become one of the most difficult tasks for gemmologists. Still today, important quantities of synthetic amethyst are present on the market, mixed with natural one. This has negative effects on costumer confidence and has prompted much research

in the distinction of natural from synthetic amethysts. In particular, arguments based on the presence or absence of certain infrared absorption bands proved promising but inconclusive to this date (see below). We propose here a new criterion, based on the existence and the width of the $3595 \, cm^{-1}$ band, which proves to be conclusive in all studied samples of known origin.

Background

Synthetic amethyst crystals grow either in a near-neutral NH_4F or in an alkaline K_2CO_3 solution (*Balitsky* et al., 1975; *Khadzi* et al., 1975). The identification of crystals grown in NH_4F solution is easy using classical gemmological techniques (study of diagnostic twinning, inclusions and in particular color zoning) or observing their specific infrared absorption bands at 3630, 3664 and $3684 \, cm^{-1}$ (*Balitsky* et al., 2004a, b). However, the vast majority of synthetic amethysts present on todays markets is grown in a K_2CO_3 solution (*Fritsch* et al., 1995; *Balitsky* et al., 2004b). Using only classical gemmological techniques it is sometimes difficult to separate this kind of synthetic amethyst from its natural counterpart (*Balitsky*, 1977, 1978, 1981; *Crowningshield* et al., 1986; *Fritsch* et al., 1987, 1988, 1989, 1995; *Stockton* et al., 1987; *Notari* et al., 2001; *Kitawaki*, 2002). This is particularly true for larger gems of good color, which neither have inclusions nor show diagnostic twinning.

Infrared absorption in the region of stretching vibrations of X–OH groups (particularly from 3000 to $3800 \, cm^{-1}$) has been suggested as a useful method to separate this kind of synthetic amethyst (in the following referred to as "synthetic amethyst") from the natural ones (*Zecchini*, 1979; *Fritsch* et al., 1987, 1988, 1995; *Smaali*, 1998; *Zecchini* et al., 1999; *Notari* et al., 2001). Generally, synthetic and natural amethysts have almost the same spectrum in this region. Both show 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 amethyst 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 et al. (2004a, b) have demonstrated that the $3543 \, cm^{-1}$ band is not as rare in natural amethyst as commonly believed and it may also be absent in some synthetic amethysts. In addition, they have demonstrated that this band reflects certain crystal growth conditions common to 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, and cannot be considered a characteristic absorption feature of synthetic amethyst.

It has been shown recently that the $3595 \, cm^{-1}$ band may be present in some synthetic amethysts (*Karampelas* et al., 2004) and absent from some natural ones (*Kitawaki*, 2002; *Balitsky* et al., 2004a, b). Thus, the interest of this study is to test under which conditions this band could be a criterion for the distinction of natural from synthetic amethyst.

Material and methods

We present here the investigations carried out on 6 samples from sources that are meaningful either for their commercial significance or because they did not satisfy criteria established in previous studies (Table 1).

The infrared absorption spectra were obtained on a Bruker 113 v FTIR spectrometer, under vacuum, at the Physics Department of Aristotle University of Thessaloniki, Greece, and on a Nicolet 20SX at the IMN, France. The spectra of uniaxial crystals (such as amethyst) in random orientation can be fully described as a linear combination of spectra taken parallel and perpendicular to the optical axis (c-axis). Therefore, for this study the crystals were cut in slabs parallel and perpendicular to the c-axis. The originality of the present study is that we established the shape of the absorptions by increasing the resolution until the shape remains the same. For this purpose, we obtained spectra of the same sample at resolutions of 4, 2, 1, 0.5 and $0.1 \, \text{cm}^{-1}$ in order to reach the shape of the absorptions. If the shape of a band does not change (narrows) any further when the resolution is increased, it is considered that the band has reached its final shape. The full width at half maximum (FWHM) of a peak 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 parallel to the linear background. This represents an estimation essentially because of the assumed linearity of the background and spectral noise. Since the optical pathlength varies with sample and orientation of the beam, the values of the absorbance have been normalized to thickness (values per millimeter; see Table 1). To obtain a good signal to noise ratio, 64 scans per sample were accumulated at $4 \, \text{cm}^{-1}$ resolution (for $0.5 \, \text{cm}^{-1}$ resolution see Table 1 also).

Thus, for each sample we collected two different sets of directional (not polarized) spectra at room temperature, with the beam direction parallel and perpendicular to the optical axis, for the range of resolutions cited above. In addition, spectra

Table 1. *Relevant data on samples of natural and synthetic amethysts from different countries showing a range of color intensities. The selected amethysts come from significant commercial sources and were selected because of 'violations' of criteria for their distinction previously proposed*

Country of origin	Color	Variety	Thickness parallel to c and perpendicular to c	Scans at $0.5 \, \text{cm}^{-1}$ resolution
Bolivia (Santa Cruz)	Dark purple	Natural (amethyst part from ametrine crystal)	5.1/4.5	128
Madagascar	Dark purple	Natural	5.1/6.1	256
Mexico (Vera Cruz)	Light purple	Natural	15.8/9.8	128
Namibia	Very dark purple	Natural	2.3/3.2	128
Russia	Light purple	Synthetic K_2CO_3	3.4/2.0	512
Russia	Moderate purple	Synthetic K_2CO_3 (amethyst part from ametrine crystal)	2.9/4.5	128

were taken in homogeneous purple areas (colorless zones are common in natural amethyst, and may have a different absorption spectrum). Every measurement was repeated in another area of the slab to ensure reproducibility of the results.

Results

The shape of the $3595\,\mathrm{cm}^{-1}$ band is obtained at a resolution of $0.5\,\mathrm{cm}^{-1}$ as there is no change in the shape for a resolution at $0.1\,\mathrm{cm}^{-1}$. The $3614\,\mathrm{cm}^{-1}$ absorption band reaches its shape even at $2\,\mathrm{cm}^{-1}$, significantly lower than the standard $4\,\mathrm{cm}^{-1}$ resolution typically used (if experimental details are given which is not always the case). The other absorption peaks of interest, at $3585\,\mathrm{cm}^{-1}$ and $3543\,\mathrm{cm}^{-1}$, reach their shape at (a standard) $4\,\mathrm{cm}^{-1}$ resolution.

Infrared absorption spectra of various test amethysts in the range 3500–$3640\,\mathrm{cm}^{-1}$ are presented in Figs. 1 to 6. Note that the wavenumber scale is expanded compared to presentations in previous publications. The spectra corresponding to the two different crystallographic orientations of the beam for two different resolutions are stacked, and offset in absorbance for clarity. In all figures, the upper spectra are taken with the beam parallel to the optical axis, and the
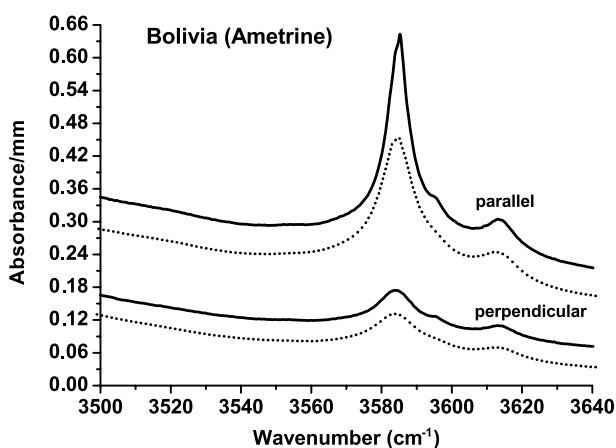

Fig. 1. Infrared absorption spectra of amethyst part of a natural ametrine from Bolivia (Santa Cruz). The $3595\,\mathrm{cm}^{-1}$ band is difficult to be detected in spectra acquired at $4\,\mathrm{cm}^{-1}$ resolution (dotted lines), whereas it is well visible at $0.5\,\mathrm{cm}^{-1}$ resolution (full lines)
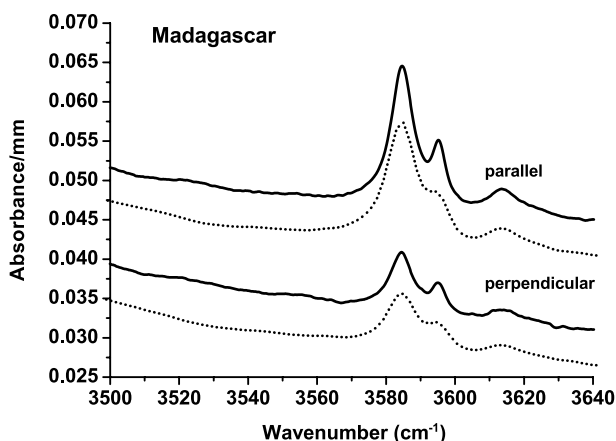

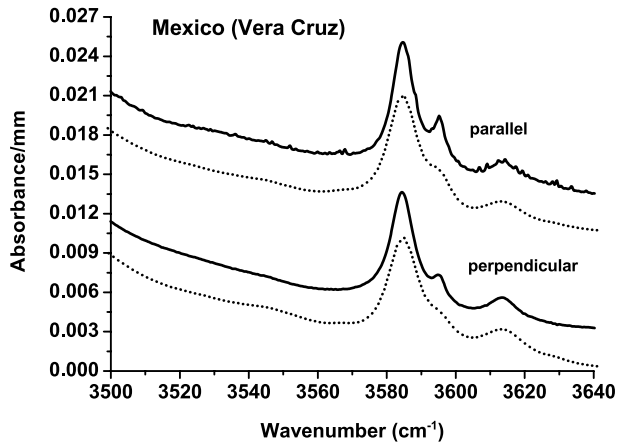Fig. 2. Infrared absorption spectra of natural amethyst from Madagascar

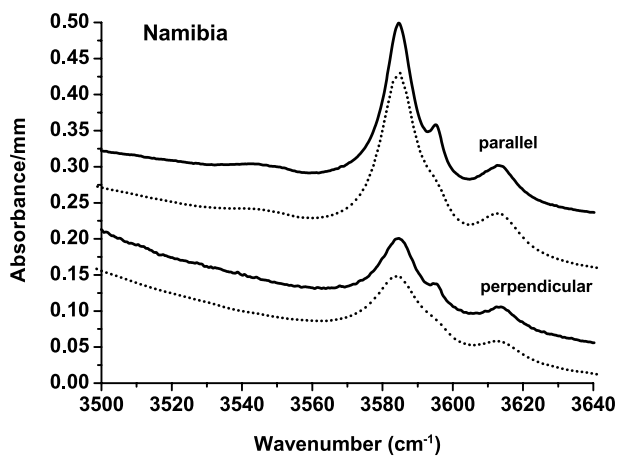Fig. 3. Infrared absorption spectra of natural amethyst from Vera Cruz (Mexico)

Fig. 4. Infrared absorption spectra of natural amethyst from Namibia. The $3595\,\mathrm{cm}^{-1}$ band is difficult to be detected in spectra acquired at $4\,\mathrm{cm}^{-1}$ resolution (dotted lines), whereas it is well visible at $0.5\,\mathrm{cm}^{-1}$ resolution (full lines)
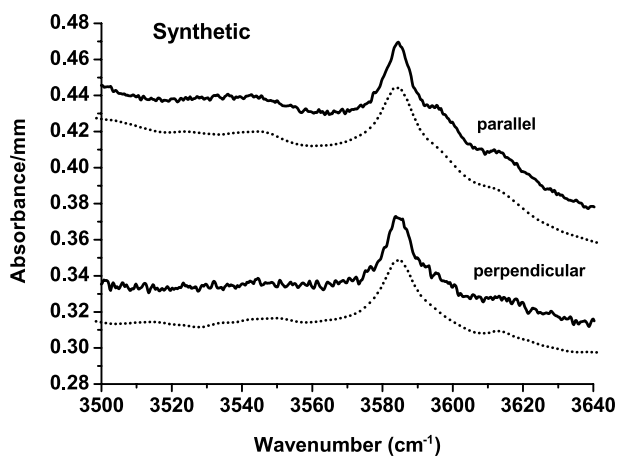

Fig. 5. Infrared absorption spectra of synthetic amethyst (K_2CO_3) from Russia. For this sample the $3595\,\mathrm{cm}^{-1}$ feature is distinct only in the spectrum taken parallel to the c-axis, with a distinct maximum for a resolution of $0.5\,\mathrm{cm}^{-1}$

lower ones with the beam perpendicular to the optical axis. The spectra with dotted lines are taken at a resolution of $4\,\mathrm{cm}^{-1}$, those with full line at a resolution of $0.5\,\mathrm{cm}^{-1}$.
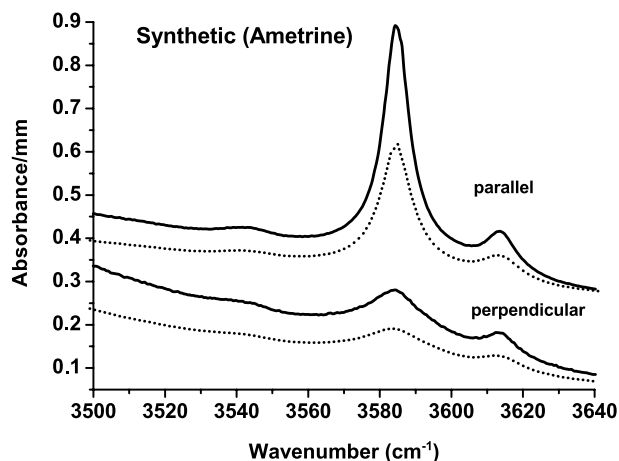
Fig. 6. Infrared absorption spectra of amethyst part of synthetic ametrine (K_2CO_3) from Russia. Note the absence of the $3595\,cm^{-1}$ band

The orientation of the beam only affects the intensities of the peaks, not their positions, and the same absorption bands are visible in both patterns. The intensities of the peaks vary from one sample to another, but are unaffected by color intensity.

We made the following observations for natural amethysts:

– The 3585 and $3614\,cm^{-1}$ bands are present in all samples (Figs. 1 to 4).
– The $3543\,cm^{-1}$ absorption band is barely visible in two of the samples (Figs. 3 and 4).
– The $3595\,cm^{-1}$ absorption band is clearly seen in two samples at $4\,cm^{-1}$ resolution (Figs. 2 and 3) but is barely visible in the other two (Figs. 1 and 4). At $0.5\,cm^{-1}$ resolution, this absorption band appears very well in the samples (Figs. 1 to 4).
– The full width at half maximum (FWHM) of the $3595\,cm^{-1}$ absorption for all the natural samples measured for both beam directions is about $3\,cm^{-1}$ ($\pm 0.5\,cm^{-1}$).

We made the following observations for synthetic amethysts:

– The absorption peaks at 3543, 3585 and $3614\,cm^{-1}$ are present in both samples (Figs. 5 and 6).
– The absorption peak at $3595\,cm^{-1}$ is seen in one of the synthetic samples (Fig. 5). This peak is more distinct in the spectra taken with the beam parallel to the optic axis. The FWHM of this peak at a resolution of $0.5\,cm^{-1}$ is about $7\,cm^{-1}$ ($\pm 1\,cm^{-1}$).

Discussion and conclusion

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 stretching vibrations of X–OH groups (which apparently depends 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. 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. This confirms previous observations (*Smaali*, 1998; *Zecchini* et al., 1999; *Balitsky* et al., 2004b). However, this is not true for one of our synthetic samples, for which the $3595\,cm^{-1}$ band is distinct only when the beam is parallel to c.

The $3543\,cm^{-1}$ absorption peak is observed in both synthetic amethysts, as expected, and in two natural ones. Therefore we confirm that the $3543\,cm^{-1}$ band is present in some rare natural amethyst. Further, these two samples serve to illustrate how samples which "violate" the criterion based on the $3543\,cm^{-1}$ band can be correctly identified using another criterion, still based on infrared absorption.

The narrowest absorption band of interest is the $3595\,cm^{-1}$ band, which attains its shape only at $0.5\,cm^{-1}$ resolution. Hence, if one uses a resolution at $4\,cm^{-1}$, as most gemmological laboratories do, one may miss this weak, but significant, $3595\,cm^{-1}$ absorption band. 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 (2002) study, but is not mentioned in *Balitsky*'s et al. (2004b) article. Therefore a resolution of $0.5\,cm^{-1}$ is necessary for the detection of the $3595\,cm^{-1}$ peak. With such a resolution, this peak has been detected in all our natural amethysts.

In addition, previous authors (*Smaali*, 1998; *Zecchini* et al., 1999) proposed that the absorption peak at $3595\,cm^{-1}$ is only observed in natural amethysts. Our observation of this peak in a synthetic amethyst, confirms previous studies (*Karampelas* et al., 2004) and indicates that this criterion must be refined.

We propose that the $3595\,cm^{-1}$ peak may be found in natural but also, rarely, in synthetic amethyst. In the latter case, its FWHM is about $7\,cm^{-1}(\pm1\,cm^{-1})$ approximately twice of that measured for natural amethyst ($3\,cm^{-1}\pm0.5\,cm^{-1}$). If the $3595\,cm^{-1}$ band is absent in the absorption spectra of an amethyst using $0.5\,cm^{-1}$ resolution, then this amethyst is synthetic. This new refined criterion works in previously ambiguous cases; in this study we included samples especially selected because they 'violated' criteria that were previously established.

Further research is needed to explore the cause for this fairly subtle difference in the infrared absorption spectrum of natural and synthetic amethyst. Previous studies (*Staats* et al., 1974; *Zecchini* et al., 1999) have linked the $3595\,cm^{-1}$ band to the presence of boron. A systematic survey of this light, difficult-to-detect impurity in amethyst may shed light on the observed differences.

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