INFRARED SPECTROSCOPY OF NATURAL VS. SYNTHETIC AMETHYST: AN UPDATE

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When microscopic identification is not feasible, FTIR spectra at high resolution (0.5 cm^{-1}) can distinguish natural and synthetic amethyst. The 3595 cm^{-1} band is characteristic of natural amethyst and has a full width at half maximum (FWHM) of 3.3 ± 0.6 cm^{-1}. In synthetic amethyst, this band is either absent or (very rarely) about twice as broad. Exceptions to this criterion include natural amethyst with pronounced near-colorless zones, which do not always display this band, and natural specimens that either have an intense, unusually broad 3595 cm^{-1} band or show total absorption in the X-OH region (3800–3000 cm^{-1}) of the spectrum.

Gem-quality amethyst is found on all continents and in various geologic environments (figure 1). Some contemporary sources are Brazil, Uruguay, Zambia, Namibia, Mexico, Russia, Arizona, Canada, Bolivia, and Sri Lanka (Shigley et al., 2010). Synthetic amethyst crystals are grown in either a near-neutral NH_4F solution (see figure DD-1 in the *G&G* Data Depository at gia.edu/gandg) or an alkaline K_2CO_3 solution (figure 2). The identification of NH_4F-grown synthetic amethyst is straightforward with standard microscopy (observation of color zoning; figure DD-2) or infrared spectroscopy (Balitsky et al., 2004b; figure DD-3). However, most synthetics in the market today are grown in K_2CO_3 solution (cited below simply as "synthetic" amethyst). Classical gemological techniques (observation of twinning, color zoning, and inclusions) can distinguish only some of these synthetics (Crowningshield et al., 1986; Notari et al., 2001, and references therein). The highest-quality products are free of inclusions, distinct color zoning, and in many cases twinning, which makes their identification more challenging.

Recent investigations have demonstrated the effectiveness of laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS) in separating natural and synthetic quartz. Plots of Ti+Cr vs. Ga are reportedly the most useful (Breeding and Shen, 2010). Unfortunately, this technique is not widely available and is too expensive to use for the identification of a common gem such as amethyst. Furthermore, overheating from the ablation laser may cause cracks in the samples (L. Klemm, pers. comm., 2011).

Infrared absorption spectroscopy in the region of X-OH stretching vibrations (i.e., 3800–3000 cm^{-1}) has long been considered useful for distinguishing natural and synthetic amethyst (Smaali, 1998; Zecchini and Smaali, 1999; Notari et al., 2001; Balitsky et al., 2004a,b; Karampelas et al., 2006, and references therein). In this region, the infrared spectra of natural and synthetic amethyst are largely similar, though they have some important differences. The specific range of interest is from 3640 to 3500 cm^{-1}, where both show absorptions at approximately 3612 and 3585 cm^{-1}. These two absorptions are probably due to vibrations caused by Al substitutions (Kats, 1962).

Earlier studies used bands at 3595 and 3543 cm^{-1}

Figure 1. Determining the natural or synthetic origin of some amethyst remains a challenge for gemologists. Shown here are three natural samples weighing 22.00-43.79 ct (at left; GIA Collection nos. 13143, 37216, and 31971) and a 4.89 ct synthetic (the emerald cut at lower right, GIA Collection no. 17239) in front of various samples of undetermined origin. Photo by Robert Weldon.

to separate natural and synthetic amethyst. The band at 3543 cm^{-1}, observed in the vast majority of lab-grown amethyst, was considered indicative of synthesis (Fritsch and Koivula, 1988). However, stones from a number of natural deposits can also show this absorption (Kitawaki, 2002), which is related to the negative rhombohedron growth sector rather than synthesis (Balitsky et al., 2004a,b). Likewise, the 3595 cm^{-1} band observed in most natural amethyst was once considered indicative of nat-

ural origin (Zecchini and Smaali, 1999, and references therein), but this band was subsequently noted in the spectra of some synthetic amethyst (Notari et al., 2001; Karampelas et al., 2005, 2006), and was reported to be absent from some natural samples (Balitsky et al., 2004a,b). FTIR measurements at high resolution (0.5 cm^{-1}) found that this band is present in all natural amethyst, but can be missed with standard 4 cm^{-1} resolution. In synthetic amethyst, this band is either absent or (rarely) when present has a

Figure 2. These K_2CO_3-grown synthetic amethysts include an unusual Russian prismatic cluster (left; 10 cm tall) and a crystal weighing more than 1 kg (right; 15 cm tall). The vast majority of synthetic amethyst in the gem market is K_2CO_3 grown. Photos by Franck Notari.

TABLE 1. Comparison of the 3595 cm⁻¹ band in natural and synthetic (K_2CO_3 grown) amethyst.

Sample no.	Origin	Type	Weight (ct)	No. scans[a]	FWHM (cm⁻¹)
		Natural			
Am008	Bolivia (Anahí)	Rough	0.4	128 or 512	2.7
Am082	Bolivia (Anahí)	Rough	4.1	128 or 1024	3.2
Am106	Brazil (Marabá)	Rough	5.3	128 or 1024	3.3
Am016	Brazil (Pau d'Arco)	Rough	0.8	200 or 300	3.5
Am448	France (St. Raphael)	Rough	1.0	128 or 512	3.0
Q022	Japan (Ishikawa)	Faceted	2.3	512 or 512	3.0
Am060	Mexico (Veracruz)	Faceted	3.0	128 or 1024	3.3
Ru007	Russia (Urals)	Rough	1.0	128 or 512	3.0
Uru007	Uruguay (Artigas)	Rough	0.4	128 or 512	3.9
Am068	USA (Four Peaks, Arizona)	Rough	3.4	128 or 1024	3.0
Am075	Zambia (Solwezi)	Rough	3.8	150 or 300	3.5
Am080	Zambia (Solwezi)	Faceted	4.0	128 or 512	3.5
Am023	Unknown	Faceted	1.2	200 or 700	5.0
Am057	Unknown	Faceted	2.9	200 or 700	5.0
		Synthetic			
Q198	Japan	Faceted	3.1	300 or 900	–
Am169	Russia	Faceted	8.5	128 or 1024	–
Am004	Russia (prismatic)	Rough	0.2	256 or 1024	–
Am585	Russia	Faceted	29.3	128 or 1024	–
Am4	Russia	Faceted	16.0	128 or 1024	–
Am1612	Russia	Faceted	8060.0	128 or 1024	–
Am177	Russia	Faceted	8.9	128 or 1024	–

[a] *At 4 or 0.5 cm⁻¹ resolution, respectively.*

FWHM value approximately two times larger than that of natural specimens (Karampelas et al., 2005, 2006).

MATERIALS AND METHODS

This study was carried out on 21 samples, 14 natural and seven synthetic. Several geographic localities were represented, including some that did not satisfy the proposed IR separation criteria given in previous studies. The natural identity of two samples of unknown origin was confirmed microscopically. All the synthetic amethyst samples in this study were grown in alkaline K_2CO_3 solutions, including rare and unusual prismatic material (figure 2, left). Nine samples were faceted and 12 were rough (for details on their size and origin, see table 1). All were obtained from reputable sources (see Acknowledgments), and none contained near-colorless zones.

Infrared absorption spectra of the faceted and some of the rough samples were acquired with a Bruker Vertex 70 FTIR spectrometer (under vacuum) at the University of Nantes, and a Varian 640 FTIR spectrometer at the Gübelin Gem Lab, both using a diffuse reflectance accessory as a beam condenser.

A Bruker 113v FTIR spectrometer (under vacuum) in the Physics Department of Aristotle University was used for measurements on some of the rough samples. The spectra were taken in random crystallographic orientation, as the bands of interest are little-affected by direction (see Karampelas et al., 2005).

Previous studies found that the true shape of the 3595 cm⁻¹ band is obtained at a resolution of 0.5 cm⁻¹ (Karampelas et al., 2005; figure DD-4). Thus, we measured the samples at 0.5 cm⁻¹, as well as at the standard 4 cm⁻¹ resolution. To obtain a high signal-to-noise ratio, multiple scans were collected (again, see table 1). When the 3595 cm⁻¹ band was present, we measured its FWHM (see figure DD-5 for more information on this process).

RESULTS AND DISCUSSION

IR absorption spectra in the 3640–3500 cm⁻¹ range are presented in figures 3–5 (and DD-6 through DD-

NEED TO KNOW

- Standard gemological testing is not always sufficient to identify synthetic amethyst.

- High-resolution (0.5 cm⁻¹) FTIR analysis has shown that the band at 3595 cm⁻¹ is present in the vast majority of natural amethyst.

- While the 3595 cm⁻¹ band can occur in synthetic amethyst, it has a much larger FWHM value than in natural specimens.

10). The spectra corresponding to the two different resolutions are stacked and offset in absorbance for clarity. In these 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 expected absorption bands at 3614 and 3585 cm⁻¹ were observed in all samples, natural and synthetic. The 3543 cm⁻¹ band was observed in five of the natural and all of the synthetic amethyst (see figure 3 and also figures DD-6 and DD-7).

The 3595 cm⁻¹ band was visible in some natural amethyst at 4 cm⁻¹ resolution and in all of them at 0.5 cm⁻¹ resolution (see figure 4 and also figures DD-8 and DD-9). In some samples, this band was very intense (figures 5 and DD-10). The band did not appear in the spectra of any of the synthetic
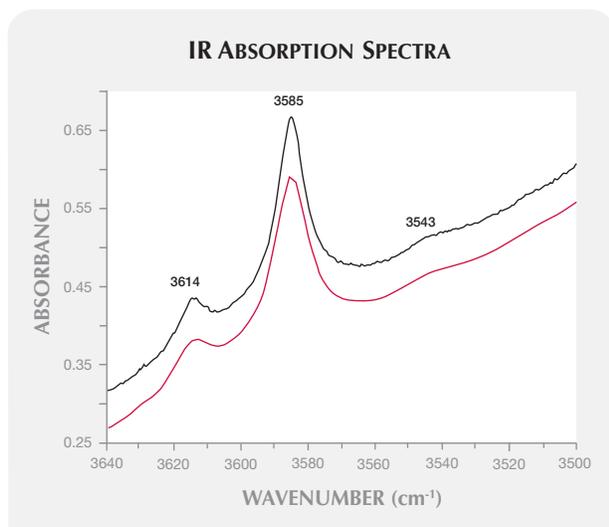
IR Absorption Spectra

Figure 3. The infrared absorption spectra of a rare 0.2 ct rough "prismatic" synthetic amethyst from Russia (Am004; see figure 2, left) are shown at resolutions of 4 cm^{-1} (red) and 0.5 cm^{-1} (black). The 3595 cm^{-1} band is not observed, but a shoulder is present at 3543 cm^{-1}.

amethyst studied here, though it did in a sample from a previous study (Karampelas et al., 2005). Some natural material from (Marabá) Brazil shows total absorption in the ~3600 to 3000 cm^{-1} region, but this has been documented as being characteristic of natural amethyst (Smaali, 1998). In a previous

Figure 4. The infrared absorption spectra of a 3.8 ct rough amethyst from Zambia (Am075) are shown at resolutions of 4 cm^{-1} (red) and 0.5 cm^{-1} (black). The 3595 cm^{-1} band is barely visible at 4 cm^{-1} but well resolved at 0.5 cm^{-1} (FWHM of 3.5 cm^{-1}).

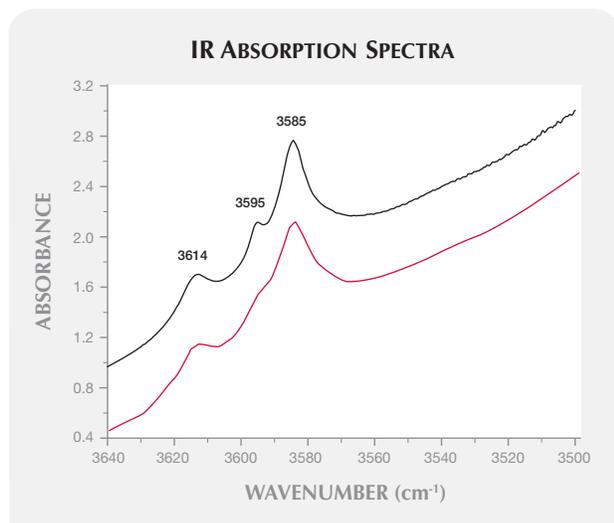**IR Absorption Spectra**

IR Absorption Spectra
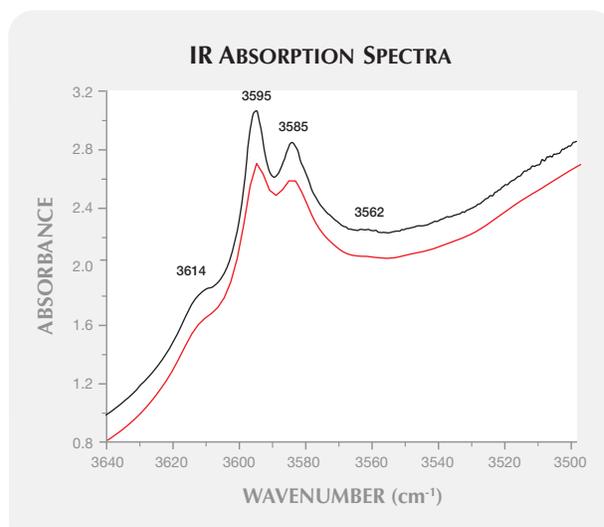
Figure 5. The infrared absorption spectra of a 2.9 ct rough amethyst of unknown origin with natural inclusions (Am057) are shown at resolutions of 4 cm^{-1} (red) and 0.5 cm^{-1} (black). The 3595 cm^{-1} band is more intense than the one at 3585 cm^{-1} in both spectra, with an FWHM of 5 cm^{-1} at 0.5 cm^{-1} resolution. A shoulder at about 3562 cm^{-1} is observed at both resolutions.

study, a sample that presented total absorption in this region was cut into two halves, which both displayed the 3595 cm^{-1} band (as well as those at 3585 and 3614 cm^{-1}; Karampelas, 2002). Some natural amethyst from other localities (e.g., Solwezi, Zambia) also shows strong absorption (i.e., a high absorption coefficient) in this region. Relatively small pieces (<10 ct) of natural amethyst with a high absorption coefficient can show total absorption in the ~3600 to 3000 cm^{-1} region. To date, no known synthetic amethyst (even large samples; figure DD-7) presents total absorption in this region. However, more samples of synthetic amethyst need to be studied to strengthen these findings.

The natural amethyst FWHM values of the 3595 cm^{-1} band at 0.5 cm^{-1} resolution are similar to those previously published (3.3 ± 0.6 cm^{-1}; Karampelas et al., 2006). Some larger 3595 cm^{-1} bands recorded in this study (FWHM: 5.0 cm^{-1}) were obtained from samples in which the 3595 cm^{-1} band was more intense than the 3585 cm^{-1} band (again, see figures 5 and DD-10). Very intense bands at 3595 cm^{-1} have also been measured in rock crystal quartzes from Norway and Japan (Nimi et al., 1999; Müller and Koch-Müller, 2009). Although some natural samples with colorless bands do not show absorption at 3595 cm^{-1}, most of those can be identified with classical gemology (e.g.,

observations of twinning and color zoning).

The exact cause of the 3595 cm⁻¹ band in amethyst is unknown (Staats and Kopp, 1974; Nimi et al., 1999; Miyoshi et al., 2005; Lameiras et al., 2009; Thomas et al., 2009; Müller and Koch-Müller, 2009). This OH⁻ band has been linked to the presence of boron in synthetic quartz (Staats and Kopp, 1974), and more recently it was observed in the spectra of B-doped synthetic quartz with an FWHM of about 7 cm⁻¹ (at 2 cm⁻¹ resolution; Thomas et al., 2009). The same OH⁻ band was attributed to structural B-related defects in the lattice of natural quartz (Müller and Koch-Müller, 2009). To the best of our knowledge, however, B-doped synthetic amethyst is not present in the gem market. Additional research is needed to find the exact cause of the slight differences in the FWHM of the 3595 cm⁻¹ band in natural and synthetic amethyst.

CONCLUSION

When classical gemological techniques are inconclusive, FTIR spectroscopy at high resolution (0.5 cm⁻¹) can provide a criterion of demonstrated validity in separating the material currently on the market (figure 6), including some rare and unusual synthetics. If there is no 3595 cm⁻¹ absorption, or if it has an FWHM of 7 cm⁻¹ or more, the sample is synthetic. If the 3595 cm⁻¹ band has a width of 3.3 ± 0.6 cm⁻¹, the sample is natural. If the 3595 cm⁻¹ band is more prominent than the 3585 cm⁻¹ band, its FWHM can be larger. Total absorption in the X-OH region (3800–3000 cm⁻¹) occurs only in natural amethyst and has not been observed to date in synthetic mate-
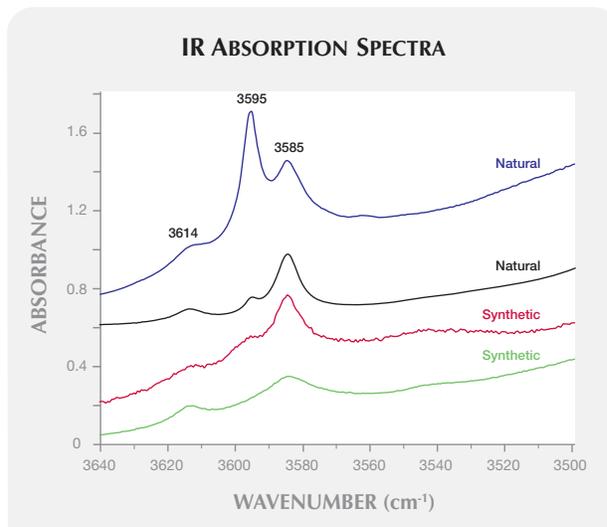

Figure 6. Shown here are infrared absorption spectra at 0.5 cm⁻¹ resolution of two synthetic amethysts (green: Am006, and red: K₂CO₃-grown from Russia, not presented in table 1 but published in Karampelas et al., 2005) and two natural specimens (black: Am060, and blue: Am023). In the synthetics, the 3595 cm⁻¹ band is either absent (green) or has an FWHM of 7 cm⁻¹ (red). Natural amethyst typically has the 3595 cm⁻¹ band with an FWHM of 3.3 ± 0.6 cm⁻¹ (black). However, some natural samples have a 3595 cm⁻¹ band that is more intense than the one at 3585 cm⁻¹, with an FWHM of 5 cm⁻¹ at 0.5 cm⁻¹ resolution (blue).

rial. The IR criteria cited above are only valid for amethyst that does not have large near-colorless zones. The 3595 cm⁻¹ band may be due to a boron-related defect in the amethyst lattice.

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