

# The Relation of FTIR Signature of Natural Colorless Quartz to Color Development After Irradiation and Heating

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## 1. Introduction

The infrared spectroscopy is a powerful technique to identify colorless quartz with potential for color development by irradiation and heating for jewelry. It is being routinely used in Brazil since 2005. In this chapter the use of FTIR for this purpose is described in detail.

Amethyst, prasiolite, citrine, and morion are gemstones widely used to make jewelry, to compose mineral collections of museums or private persons, or to decorate homes and offices. They are all alpha quartz (Dana et al., 1985) and the differences between them are very small. The natural quartz always has trace elements in its crystal structure, such as aluminum, iron, hydrogen, lithium, sodium, and potassium. The content of these trace elements is important for color development. But without exposure to ionizing radiation, these trace elements are not able to produce colors in quartz.

Since the discovery of radioactivity, it has become clear that the color of several minerals, including the quartz, can be modified by their exposure to radiation emitted by radioactive substances (Nassau, 1978 and Nassau, 1980). An amethyst is colorless quartz with small contents of aluminum, iron, hydrogen, sodium, lithium, and potassium. It was formed as a result of a hydrothermal process similar to the one used to produce cultured quartz for the electronic industry. The hydrothermal solution and the environment of the amethyst (e.g., feldspar) may be rich in potassium. Potassium is a natural radioactive element due to its  $^{40}\text{K}$  isotope, which emits gamma rays with an energy of 1.46 MeV and has a half life of 1,260,000,000 years. Other natural radioactive elements (thorium and uranium) can also provide the radiation. Such an exposure during a geologic time span can accumulate irradiation doses high enough to produce the violet color of amethyst. However, if the natural irradiation was weak, the amethyst remains colorless. It can be exposed to gamma rays of a man-made  $^{60}\text{Co}$ -source to develop intense violet colors. The same is true for prasiolites. Other colors of quartz can be formed by a similar process.

Jewelry demands tons of colored quartz that cannot be found in nature. It is necessary to extract colorless quartz from nature and submit it to irradiation and heating. The problem is separating the quartz that can develop colors of commercial value from the quartz which cannot. Usually this separation is done through irradiation tests of representative samples.

But these tests can take weeks, because the samples need to be sent to an irradiation facility to be irradiated to varying doses. The irradiated samples then need to be sent back to the owner, who must perform the heating (in some cases) and evaluate the quality of color. Another problem is that some irradiators do not inform the applied doses.

The FTIR signature of the colorless quartz can be very valuable in indicating whether or not it can develop colors. Through a previous correlation with the results of irradiation tests (Nunes et al. 2009), it is possible to forecast the color that will be achieved after an irradiation dose. This analysis takes only a few minutes and can be performed close to the mining site if a FTIR spectrometer is available.

Infrared measurements were widely reported in electrodiffusion studies of quartz with alkalis (Martin, 1988). The purpose of these studies was to understand the electronic performance of cultured quartz for the electronic industry. There are few studies concerning color formation. The region of interest is from 2400  $\text{cm}^{-1}$  to 3650  $\text{cm}^{-1}$ . Table 1 shows the bands that can be observed in colorless quartz at room temperature.

Band number	Wavenumber ( $\text{cm}^{-1}$ )	Remark
1	2499	Strong, always present
2	2600	Strong, always present
3	2677	Strong, always present
4	2771	Strong, always present
5	2935	Small band, always present
6	3063	Small band, always present
7	3202	Small band, always present, Si-O overtone
8	3303*	Small band, always present, Si-O overtone
9	3381*	Al-OH related
10	3433*	Al-OH/ $\text{Na}^+$ related
11	3483*	Al-OH/ $\text{Li}^+$ related
12	3404*-510* doublet	Not assigned
13	3441* and 3585 doublet	3441 $\text{cm}^{-1}$ is a broad band
14	3441* and 3585 doublet	3441 $\text{cm}^{-1}$ is a broad band with strong absorption above 3000 $\text{cm}^{-1}$
15	3595	Not assigned

(\*) The position of these bands may vary within  $\pm 10 \text{ cm}^{-1}$

Table 1. FTIR bands observed in the spectrum of colorless quartz at room temperature

## 2. Acquisition of the FTIR spectra for determination of the potential for color development

The spectrum should be acquired in crystals, because some bands in the 2400 to 3650  $\text{cm}^{-1}$  region are too weak to be resolved in pulverized samples. A thick fragment of a quartz

crystal (1 to 5 cm) can be usually used to perform this measurement. The exception to this is prasiolite, which has a strong absorption. In this case, a thin fragment (less than 1 mm) should be used. The fragments can be obtained by a crude and rapid process, like beating the sample with a hammer. It is not necessary to orient the fragments of the crystals. One should protect the eyes with glass and the hands with gloves when beating the samples, because the quartz fragments are very sharp.

The resolution of the FTIR measurement should be at least  $4\text{ cm}^{-1}$  with a minimum of 16 scans. In case a high noise is observed, a relocation of the sample in the measurement compartment is required.

Since there is no control of the fragment thickness, the absolute absorbance values are meaningless. All the analysis should be performed on normalized spectra. The normalization is carried out relative to the bands at  $2499$  to  $2771\text{ cm}^{-1}$ , because they are related to the Si-O bond, and are not affected by the irradiation or heating, and are present in all samples. The height of one of these bands is taken equal to 1 (in the spectra of these Chapter, the band at  $2677\text{ cm}^{-1}$  was chosen) and the absorption at all wave numbers is proportionally corrected.

A background of infrared absorption that rises, falls, or is constant for wave numbers above  $3000\text{ cm}^{-1}$  can be observed (see Figure 1). This background is used to calculate the spectra baselines by fitting a third-order polynomial in the range of  $4100$  to  $5300\text{ cm}^{-1}$ , where no bands are observed, and then subtracted from the normalized spectra.

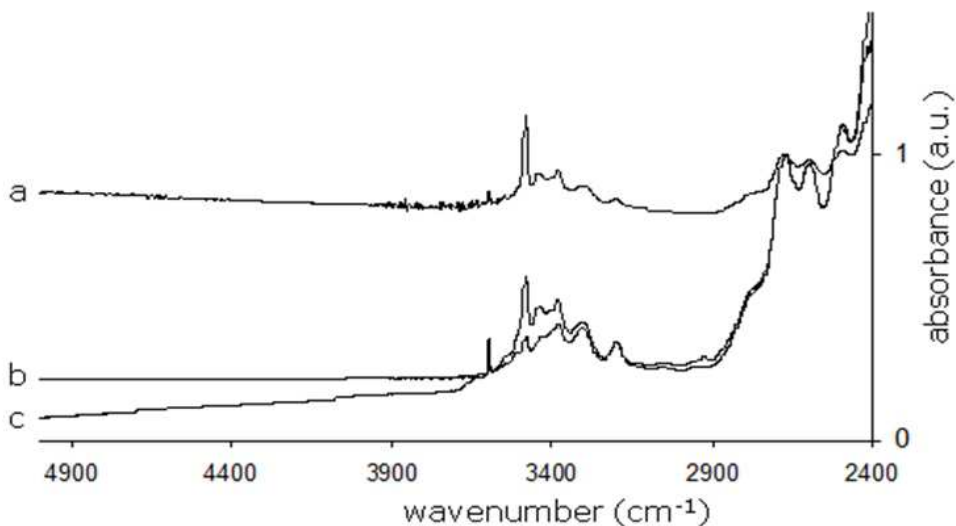


Fig. 1. Examples of colorless samples of natural quartz that show a background of infrared absorption that rises (line a), is constant (line b), or falls (line c) for wavenumbers above  $3000\text{ cm}^{-1}$ . The typical noise between  $3600$  and  $4000\text{ cm}^{-1}$  is observed in a and b. (Nunes et al., 2009).

The rising background is attributed to internal turbidity of the samples or to micro-inclusions (Hebert and Rossman, 2008). Many samples show a noise in the range of 3600 to 4000  $\text{cm}^{-1}$  that also is attributed to micro inclusions.

### 3. The FTIR spectrum relationship to color formation

#### 3.1 Smoky, morion, green gold, and brown quartz

The FTIR signature of this kind of quartz is shown in Figure 2. The band at 3483  $\text{cm}^{-1}$  is related to Al-OH/Li<sup>+</sup> and plays an important role in color formation. It appears prominent in the samples that develop colors of commercial value after irradiation and heating.

After irradiation, these samples become smoky or black (morion). The band at 3483  $\text{cm}^{-1}$  decreases and the bands at 3389 and 3313  $\text{cm}^{-1}$  increase (see Figure 3). The band at 3483  $\text{cm}^{-1}$  partially recovers after heating. These samples become green gold, yellow, or brown after heating, depending on the irradiation doses. A new band appeared at 3539-3451  $\text{cm}^{-1}$  in colored samples. If the band at 3483  $\text{cm}^{-1}$  is weak in the colorless sample, it may become colorless or weak in color after irradiation and heating.

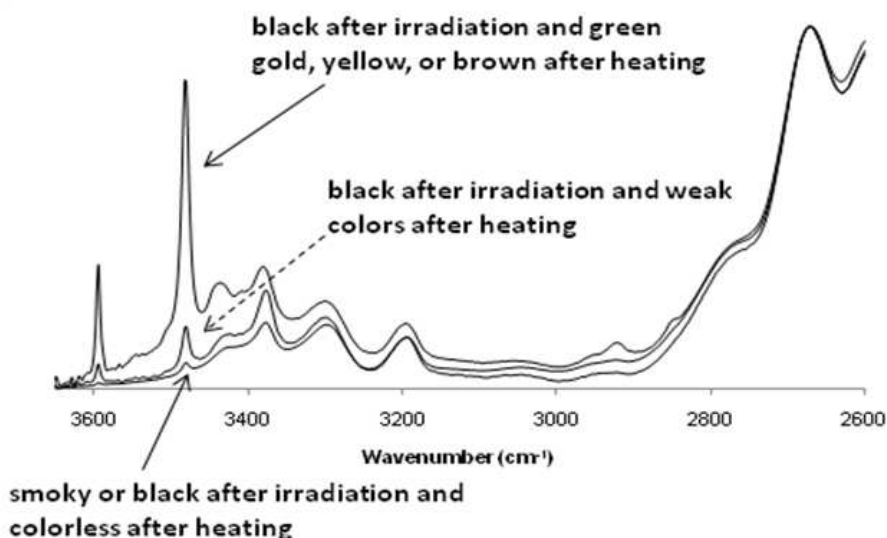


Fig. 2. The FTIR signature of quartz that become smoky or black after irradiation and green gold, yellow, or brown after heating.

One observes that the ultraviolet irradiation can partially recover the spectrum before radiation and bleach the smoky or black color developed by the  $\gamma$ -irradiation (see Figure 4). The colors developed after heating are resistant to ultraviolet rays.

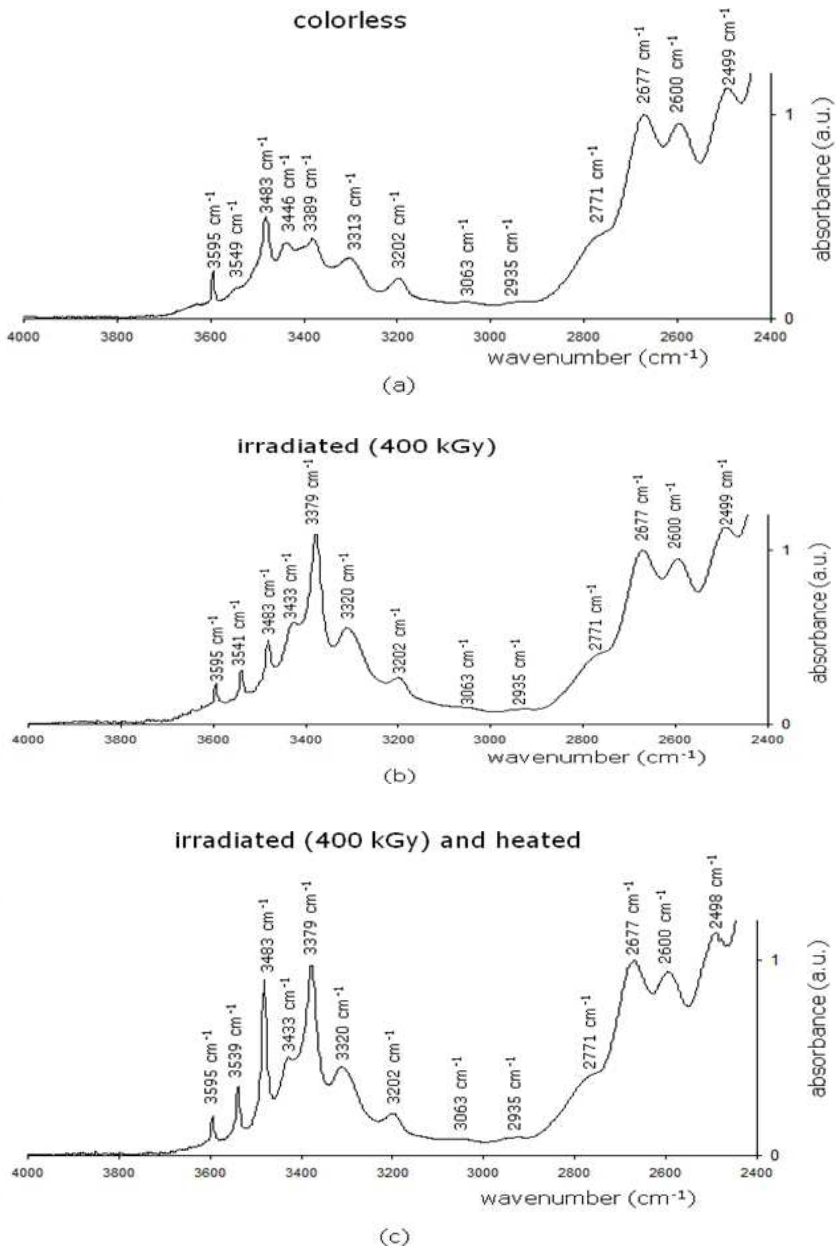
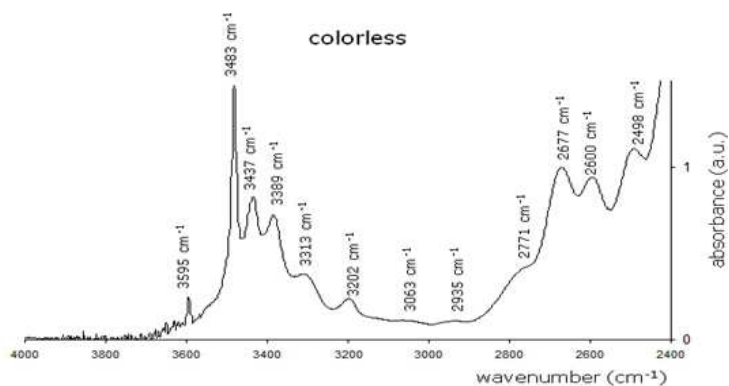
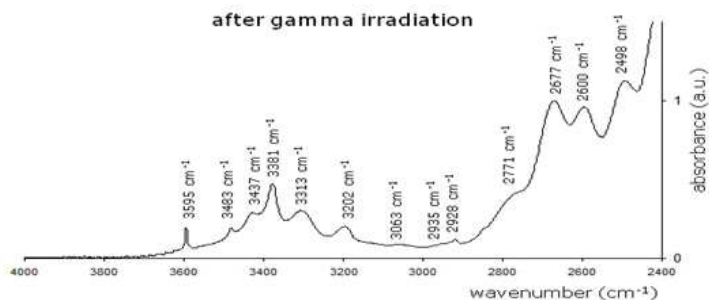


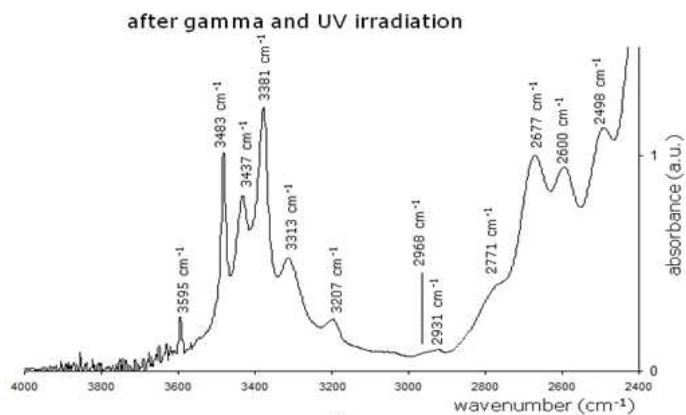
Fig. 3. The influence of irradiation and heating: (a) colorless, before  $\gamma$ -irradiation; (b) black, after  $\gamma$ -irradiation; (c) colored (greenish, greenish yellow, yellow, or brown), after irradiation and additional heating (Nunes et al., 2009).



(a)



(b)



(c)

Fig. 4. The influence of ultraviolet irradiation: (a) colorless, before  $\gamma$ -irradiation; (b) black, after  $\gamma$ -irradiation; (c) lightly smoky, after  $\gamma$ -irradiation and UV irradiation (exposure to a 5 kW iron iodide lamp for 60 minutes, with the sample temperature kept below 333 K by air ventilation). (Nunes et al., 2009).

### 3.2 Amethyst and prasiolite

The signature of colorless quartz that becomes amethyst or prasiolite after irradiation is shown in Figure 5. Both have the 3441  $\text{cm}^{-1}$  and 3585  $\text{cm}^{-1}$  doublet. The band at 3441  $\text{cm}^{-1}$  is very broad. The difference between these gems is their absorption in this region. The prasiolite has a stronger absorption in the 2700  $\text{cm}^{-1}$  to 3650  $\text{cm}^{-1}$  range. There is a transition zone (the spectrum in the middle in Figure 5), where the quartz is neither amethyst nor prasiolite. In this zone the colorless quartz cannot develop colors of commercial value.

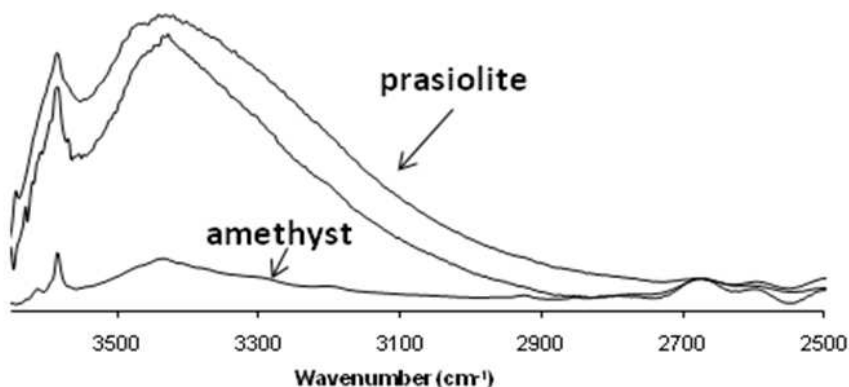


Fig. 5. The FTIR signature of colorless quartz that become amethyst or prasiolite after irradiation.

Figure 6 shows spectra at room temperature and at 93 K of a colorless sample of quartz that develops the violet color after irradiation (amethyst). At low temperature the bands appear higher, narrower, and shifted up to 10  $\text{cm}^{-1}$  (Fritzgerald et al., 2006). The broad band at 3441  $\text{cm}^{-1}$  at room temperature is decomposed into several bands at 93 K. The absorbance between 3450 and 3575  $\text{cm}^{-1}$  is lower at 93 K, indicating that there are either no bands or only bands of very low intensity in this region. Figure 6c shows the spectrum at 93 K after irradiation (violet). With respect to the colorless spectrum, the irradiated one shows a band at 3306  $\text{cm}^{-1}$ , a remarkable growth of the band at 3365  $\text{cm}^{-1}$ , a slight decrease of the band at 3580  $\text{cm}^{-1}$ , and the growth of a small band at 3549  $\text{cm}^{-1}$ .

Ultraviolet rays can bleach the colors of amethyst and prasiolite developed after irradiation. Prasiolites become grayish-green after irradiation. Through a short exposition to ultraviolet rays, the grayish component can be bleached out.

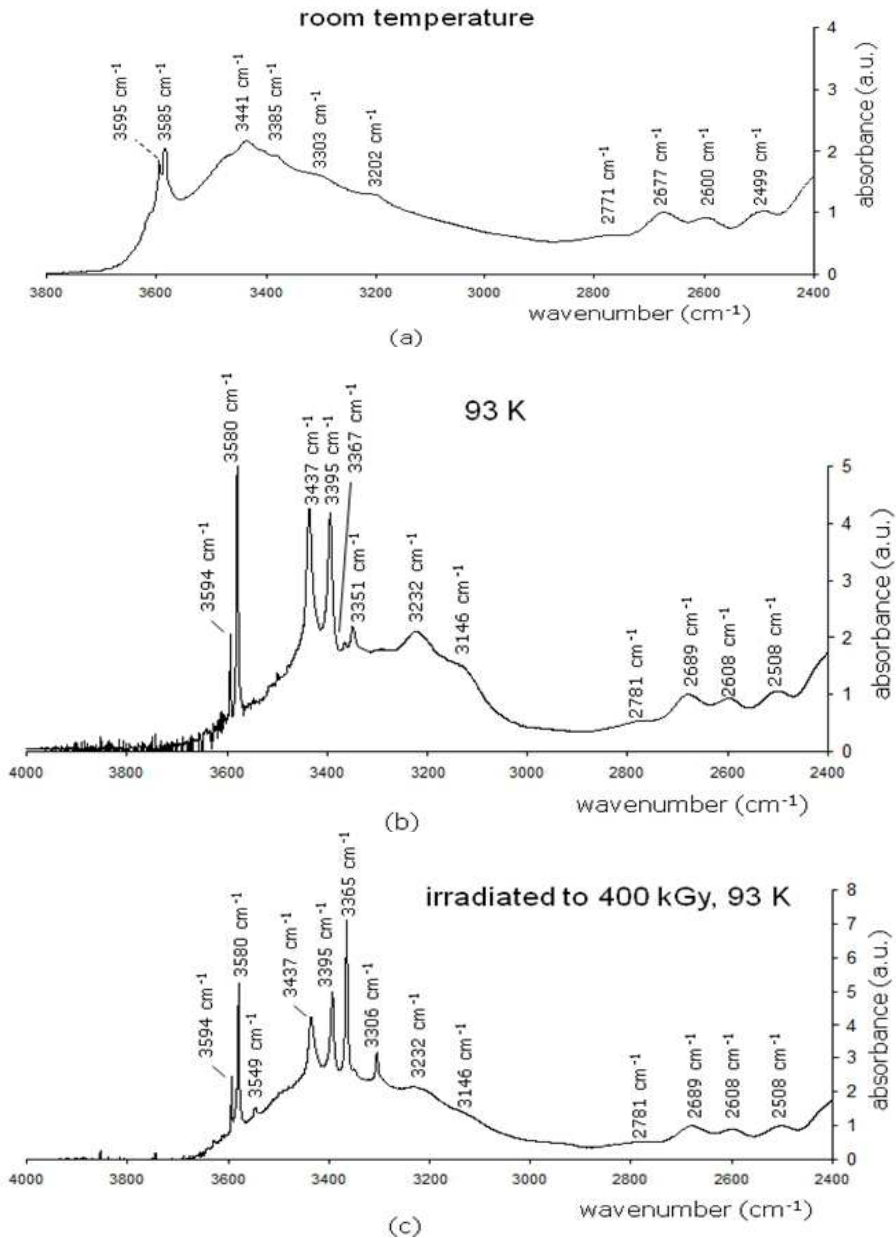


Fig. 6. Infrared spectra of a colorless sample of quartz that becomes violet (amethyst) after  $\gamma$ -irradiation: (a) at room temperature, before  $\gamma$ -irradiation (colorless); (b) at 93 K, before  $\gamma$ -irradiation (colorless); (c) at 93 K, after  $\gamma$ -irradiation (violet). (Nunes et al., 2009).



### 3.3 Olive green quartz

There is a kind of quartz that becomes grayish-olive green after irradiation. The grayish component can be bleached out through a brief period of heating. Its FTIR signature is shown in Figure 7. It shows a pair of bands at 3404 and 3510  $\text{cm}^{-1}$ . Ultraviolet rays can bleach the color developed by these samples.

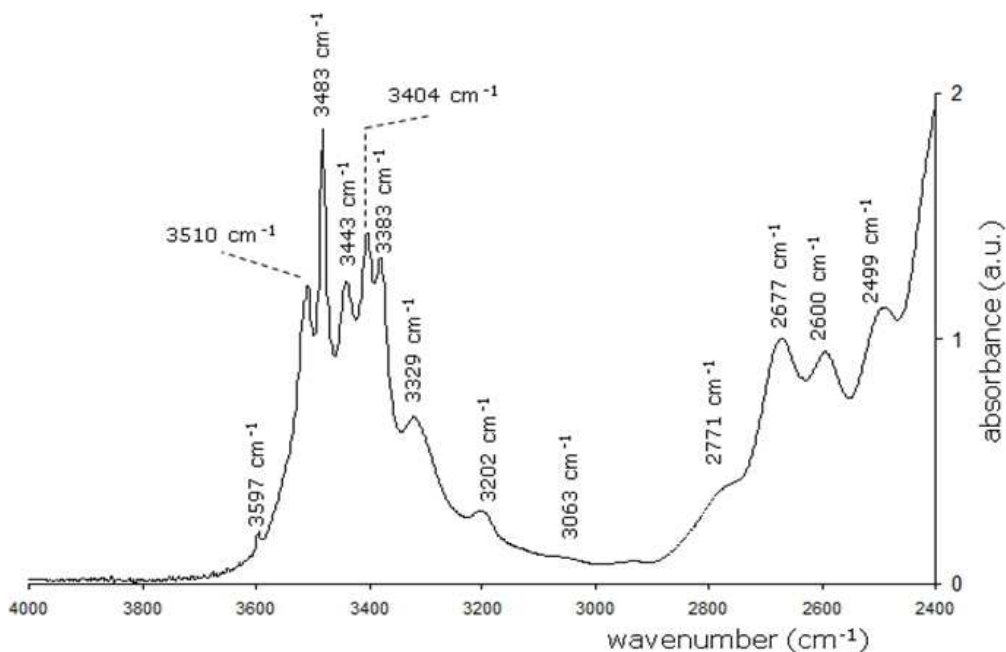


Fig. 7. The spectrum at room temperature of colorless quartz that becomes grayish-olive green after  $\gamma$ -irradiation and olive green after additional short heating. (Nunes et al., 2009).

## 4. Quantitative analysis of the FTIR spectra

### 4.1 The lithium factor

The lithium factor can be calculated from the spectra shown in Figure 2. The bands at 3483, 3446, and 3339  $\text{cm}^{-1}$  are, respectively, related to lithium, sodium, and hydrogen. Figure 8 shows how the lithium factor,  $f_{Li}$ , is calculated. One observes that samples with  $f_{Li} > 2.0$  develop intense colors. If  $1.0 \leq f_{Li} \leq 2.0$ , the samples can develop intense colors, depending on the area below the spectrum between 3000  $\text{cm}^{-1}$  and 3600  $\text{cm}^{-1}$ . If  $f_{Li} < 1.0$ , the samples develop weak colors with no commercial value.

The area is calculated according to the following formula:

$$\text{area} = \int_{3000\text{cm}^{-1}}^{3600\text{cm}^{-1}} h(w) \cdot dw \quad (1)$$

where  $h(w)$  is the high in a.u. at the wave number  $w$ . The area gives a measured of the content of trace elements in the sample (see Figure 9), the greater the area, the higher the content of trace elements.

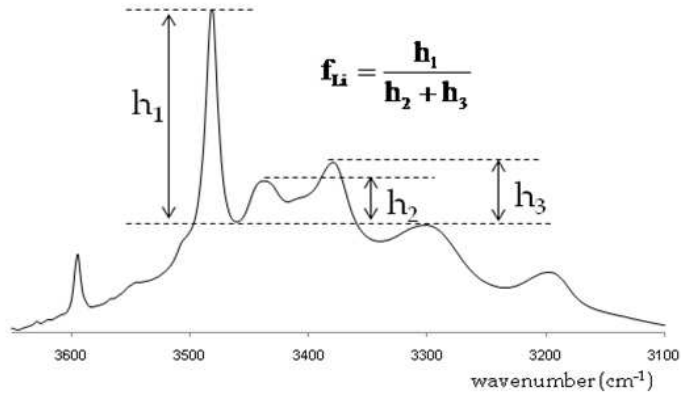


Fig. 8. Calculation of the lithium factor,  $f_{Li}$ .  $h_i$  are the heights measured in a.u. in normalized spectra after subtraction of the base line.

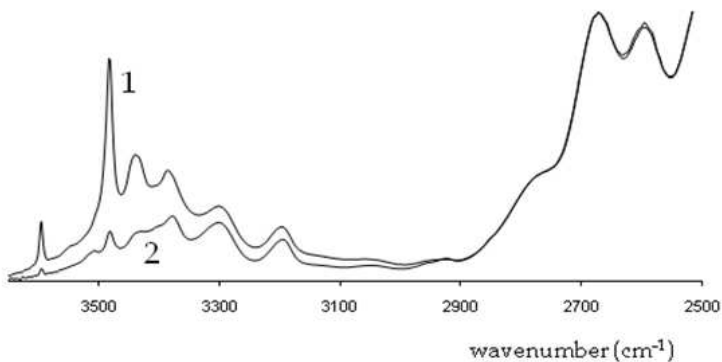


Fig. 9. In sample 1,  $f_{Li} = 2.1$  and area = 126 u.a.cm<sup>-1</sup> and develops intense colors. In sample 2,  $f_{Li} = 0,3$  and area = 69 u.a.cm<sup>-1</sup> and develops weak colors.

Table 2 summarizes the potential for color development according to the lithium factor, area, and doses of  $\gamma$ -ray exposure.

$f_{Li}$	area (u.a.cm <sup>-1</sup> )	dose (kGy)	color development
< 1.0	independent	< 100	grayish after irradiation and weak colors after heating
		> 100	black after irradiation and weak colors after heating
1.0 ≤ $f_{Li}$ ≤ 2.0	< 100	< 100	grayish after irradiation and weak colors after heating
		> 100	black after irradiation and weak colors after heating
	≥ 100	60 - 100	black after irradiation and greenish-yellow after heating
		100 - 200	black after irradiation and yellow after heating
		> 200	black after irradiation and brown after heating
> 2.0	independent	60 - 100	black after irradiation an greenish-yellow after heating
		100 - 200	black after irradiation and yellow after heating
		> 200	black after irradiation and brown after heating

Table 2. Potential of color development according to the lithium factor and area.

#### 4.2 The amethyst factor

The amethyst factor can be calculated from the spectra shown in Figure 5. Figure 10 shows how the amethyst factor,  $f_a$ , is calculated.  $h_1$  is the height of the band at 3441 cm<sup>-1</sup>, and  $h_2$  is the height of the minimum between 3441 and 3585 cm<sup>-1</sup>. One observes that samples in which  $f_a > 3.3$  develop violet colors. If  $2.7 \leq f_a \leq 3.3$ , the samples can develop colors between violet and green with no commercial value. If  $f_a < 2.7$ , the sample develops the green color of prasiolite. However, it is also important to observe the area, as shown in Table 3.

#### 5. Mechanism of color formation

Gamma rays can remove electrons from their positions within the quartz crystal lattice, creating electron-electron hole pairs. The removed electrons are trapped in interstitial positions and the electron holes have a high mobility within the crystal lattice. The localized electric charge unbalances created by the electron holes together with the trapped electrons contribute to their rapid recombination. For this reason, pure quartz remains unchanged after  $\gamma$ -ray irradiation.

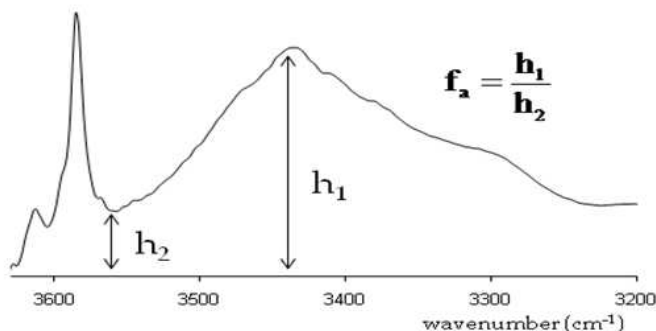
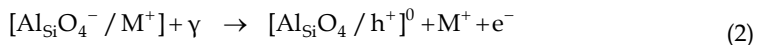


Fig. 10. Calculation of the lithium factor,  $f_{Li}$ .  $h_i$  are the heights measured in a.u. in normalized spectra after subtraction of the base line.

$f_a$	area (u.a.cm <sup>-1</sup> )	dose (kGy)	color development
< 2.7	< 900	> 600	grayish-green after irradiation and weak green (prasiolite) after exposure to ultraviolet rays and colorless or weak yellow after irradiation and heating
	> 900		grayish-green after irradiation and green (prasiolite) after exposure to ultraviolet rays and colorless or yellow (citrine) after irradiation and heating
$2.7 \leq f_a \leq 3.3$	independent	independent	no definition between violet and green
> 2.7	< 200	> 200	weak violet after irradiation and colorless or weak yellow (citrine) after irradiation and heating
	> 200		violet after irradiation and colorless or yellow (citrine) after irradiation and heating

Table 3. Potential of color development according to the amethyst factor and area.

But if  $Al^{3+}$  replaces  $Si^{4+}$  in certain positions within the quartz lattice ( $Al_{Si}$ ), the situation is quite different, because there is one unpaired electron in the  $Al_{Si}O_4^-$  tetrahedron. One electron should be donated by a hydrogen or alkaline atom. The positive hydrogen or alkaline ion should remain in the vicinity bounded by the electron attraction of the  $[Al_{Si}O_4]$ -tetrahedron. The OH- vibrations modes in quartz are influenced by these bounded positive ions and are observed in the infrared spectrum (see Table 1). If an electron is removed by a gamma photon from the  $[Al_{Si}O_4]$  tetrahedron, the positive ion becomes unbounded and free to diffuse in the crystalline lattice, according to



where  $\text{M}^+$  is the positive ion ( $\text{H}^+$ ,  $\text{Li}^+$ , or  $\text{Na}^+$ ),  $\text{h}^+$  is an electron hole, and  $\text{e}^-$  is an electron. Hydrogen and alkali ions linked to Al-associated defects are known to reside in the c-axis channels of quartz crystal lattice, which contribute to their mobility (Walsby et al., 2003). The  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  is the  $[\text{Al}_{\text{Si}}\text{O}_4]^-$  after the removal of one electron. It is called a color center and is related to the absorption of light in the visible spectrum, producing the colors gray to black after irradiation. The electron hole remains trapped in this center, but it can move within the oxygen electron clouds around the  $\text{Al}_{\text{Si}}$ .

The bands at 3303 and 3381  $\text{cm}^{-1}$  are related to aluminum and hydrogen. The  $\text{H}^+$  should be bounded to oxygen in the vicinity of aluminum due to the electrostatic attraction, forming a hydroxyl (Bahadur, 1995). It has a very high mobility in the quartz lattice once it is free to diffuse, due to the formation of the  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center. It can combine with an interstitial electron and form a hydrogen atom, which also has a high mobility in the lattice. The hydrogen may eventually approach the vicinity of another  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center, donate its electron, and become attached to an oxygen. These processes should occur at room temperature, because the bands at 3303 and 3381  $\text{cm}^{-1}$  are not affected or can even grow after irradiation if hydrogen atoms were interstitially present in the lattice before the irradiation.

The lithium is a light and small ion. Once it is free to diffuse due to the formation of a  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center, it can diffuse within the quartz lattice with moderate mobility. The correspondent infrared band at 3483  $\text{cm}^{-1}$  should decrease after irradiation (see Figure 4). Upon heating, the  $\text{Li}^+$  can move farther from the vicinity of the aluminum atom. At the same time, the removed electrons can return to the aluminum vicinity and combine with  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center, forming an  $[\text{Al}_{\text{Si}}\text{O}_4]^-$  center, which is probably related to the band at 3539 – 3451  $\text{cm}^{-1}$  observed in greenish-yellow, yellow, or brown samples (see Figure 4c). This band was also reported in citrine (obtained by the heating of amethyst) (Maschmeyer et al., 1980). With prolonged heating, the color is bleached because  $\text{Li}^+$  can approach the  $[\text{Al}_{\text{Si}}\text{O}_4]^-$  center and form the configuration it had before the irradiation,  $[\text{Al}_{\text{Si}}\text{O}_4/\text{Li}^+]^0$ .

The sodium is a heavy and large ion. Once it is free to diffuse, it cannot move away from the vicinity of an aluminum atom. It attracts removed electrons to its vicinity, that can combine with the  $[\text{Al}_{\text{Si}}\text{O}_4]^-$  center. The infrared band related to sodium should remain nearly unaffected by the irradiation. This is the band at 3437  $\text{cm}^{-1}$  at room temperature. Upon heating, the electrons which remained at interstitial positions after the irradiation are attracted by the  $\text{Na}^+$  ions and combine with the  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center. This ion cannot contribute to the formation of color after heating.

The potassium ion is very large and heavy ion. It probably cannot exist in the vicinity of an aluminum atom because great distortions of the lattice would be created. Figure 11 depicts the mechanism of color formation in quartz.

The ultraviolet irradiation can move the trapped interstitial electrons that were displaced by the gamma rays. They may eventually combine with the  $[\text{Al}_{\text{Si}}\text{O}_4/\text{h}^+]^0$  center, forming an  $[\text{Al}_{\text{Si}}\text{O}_4]^-$  center, which in turn combines with the positive ion within its vicinity. The ultraviolet irradiation can recover the infrared spectrum produced by the gamma irradiation (see Figure 4) and bleach the resultant colors. The colors produced by heating cannot be

bleached by ultraviolet irradiation because  $\text{Li}^+$  cannot be brought back to the vicinity of aluminum at temperatures below 453 K.

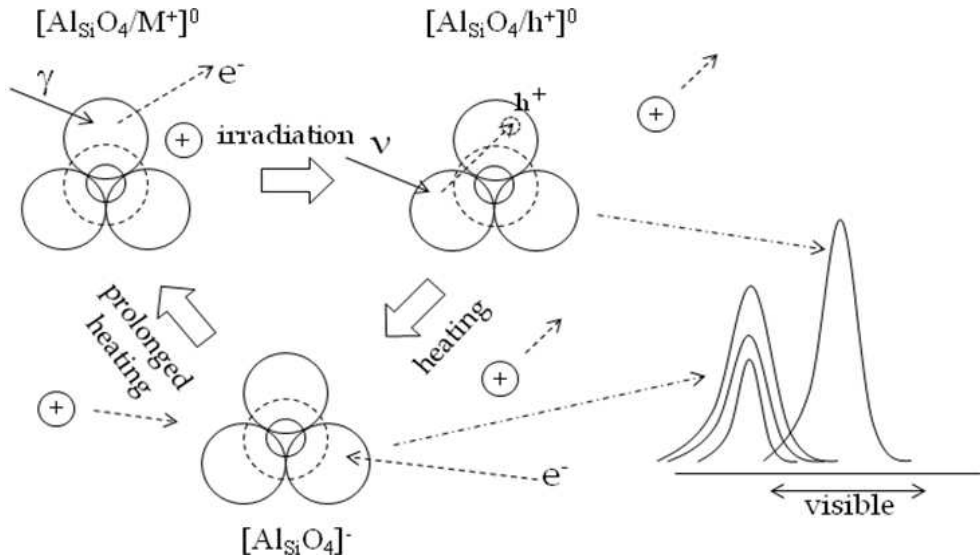


Fig. 11. Mechanism of color formation in quartz. The large circles represent oxygen atoms; the small solid circles represent aluminum atoms; the small dashed circle represents an electron hole,  $h^+$ ; the circles with + are the charge compensator ions ( $\text{H}^+$ ,  $\text{Li}^+$ , or  $\text{Na}^+$ );  $\gamma$  and  $\nu$  are, respectively, a gamma photon and a photon within the visible spectrum. The  $[\text{AlSiO}_4/h^+]^0$  center absorbs light in the visible region; the  $[\text{AlSiO}_4]^-$  center has an absorption band in the ultraviolet with a tail in the visible region, which is responsible for color formation.

If  $\text{Fe}^{3+}$  replaces  $\text{Al}^{3+}$ ,  $\text{Fe}_{\text{Si}}$ , the situation is more complex. The ionic radius of  $\text{Fe}^{3+}$  is large enough to cause substantial distortions in the tetrahedral configuration of the quartz lattice.  $\text{Al}^{3+}$  has an electronic configuration similar to  $\text{Si}^{4+}$  (both have the  $[\text{Ne}]$  configuration), whereas  $\text{Fe}^{3+}$  has a very different one,  $[\text{Ar}]3d^5$ . This difference causes additional distortions in the lattice in the vicinity of an iron atom. These distortions caused by the iron substitution for silicon provides the condition for  $\text{K}^+$  to be accommodated in its vicinity. Potassium was reported in prasiolite and amethyst (Hebert and Rossman, 2008). The bands that grew after irradiation of amethyst (at 3306 and 3365  $\text{cm}^{-1}$ , see Figure 6) are related to aluminum and hydrogen. They are probably also related to the formation of  $[\text{AlSiO}_4/h^+]^0$  centers. The lattice distortions may cause a shift in the absorption spectrum of the  $[\text{AlSiO}_4/h^+]^0$  center to larger wavelengths and produce the violet and green colors after  $\gamma$ -irradiation of colorless quartz

(see Figure 12). If the concentration of aluminum and lithium are high, the heating of irradiated violet or green quartz can produce yellow colors by a mechanism like the one previously described.

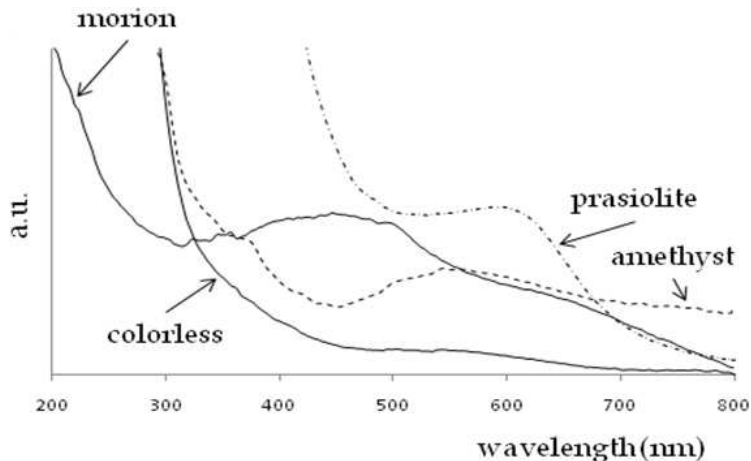


Fig. 12. Absorption spectra of fragments of colorless quartz, morion (black), amethyst (violet), and prasiolite (green) in the visible and ultraviolet range. The maximum absorption in the visible range is shift to larger wavelengths from morion (450 nm) to amethyst (467 nm) and to prasiolite (610 nm).

The nature of the bands at room temperature at 3404, 3510, 3585, and 3595  $\text{cm}^{-1}$  is not yet assigned. The band at 3585  $\text{cm}^{-1}$  is probably related to iron, because this is a trace element in amethyst and prasiolite.

## 6. Final remarks

The infrared spectrum at all colorless samples of natural alpha quartz show bands at 2499, 2600, 2677, and 2771  $\text{cm}^{-1}$ . Two small bands are also observed at 2935 and 3063  $\text{cm}^{-1}$ . The samples that do not develop colors after irradiation show bands at 3202 and 3304  $\text{cm}^{-1}$  (overtones of the Si-O bond). The samples that become grayish to black after irradiation show three more bands at 3381, 3433, and 3483  $\text{cm}^{-1}$ . This last band is related to the development of the colors greenish-yellow, yellow, or brown after heating. The intensity of these colors is proportional to the intensity of this band. The samples that become grayish-olive green after irradiation show, in addition to the former bands, a pair of bands at 3404 and 3510  $\text{cm}^{-1}$ . The samples that become violet (amethyst) after irradiation show a broad band at 3441  $\text{cm}^{-1}$  and a band at 3585  $\text{cm}^{-1}$ . The samples that become grayish-green after irradiation and green (prasiolite) after short exposure to ultraviolet rays also show the band at 3585  $\text{cm}^{-1}$ , but the broad band at 3433  $\text{cm}^{-1}$  is more intense. These samples show strong absorption of infrared radiation in the range above 2700  $\text{cm}^{-1}$ . Finally, some samples of quartz show a band at 3595  $\text{cm}^{-1}$  that does not seem related to the formation of any color.

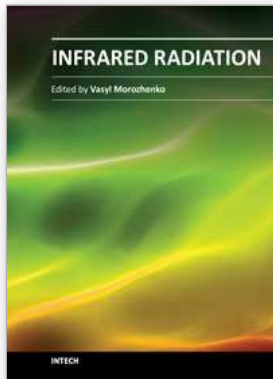
All colors developed after irradiation can be bleached by ultraviolet irradiation because they are due to the dislocation of electrons in the

quartz lattice. The colors developed after irradiation and heating cannot be bleached by ultraviolet irradiation because the heating causes the diffusion of lithium in quartz lattice. The band at  $3539 - 3451 \text{ cm}^{-1}$  is probably related to the colors obtained after irradiation and heating. A quantitative analysis can be performed on the FTIR spectrum of natural quartz in order to evaluate the potential of color development after irradiation and heating. A similar analysis can also be performed in other gemstones whose colors need to be enhanced by irradiation, such as topaz, beryl, spodumene, and tourmaline and should be the subject of future researches.

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