

GAMMA RADIATION OF QUARTZ FROM ENTRE RIOS (SC) AND QUARAÍ (RS)

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ABSTRACT

The availability of gamma ray irradiators in Brazil increased the possibilities of treatments of gemstones for color enhancements. One of the minerals with a very high potential of these treatments is quartz, a very widespread mineral with many colored commercial varieties.

A specific variety of quartz showing a green color in nature or induced artificially by radiation gamma (⁶⁰Co) is quite rare. In Brazil the widely scattered geode occurrences along a 600 km stretch from Quaraí at Brazil southernmost tip to Uberlândia in Minas Gerais is one of these. Quartz from these occurrences have been formed by strong hydrothermal activities. That way much quartz crystals showed a very fast growth history facilitating the formation of growth defects and the uptake of water in form of micro inclusions, molecular water, silanol (Si-OH) and OH. In the present work the material analyzed is from hydrothermal regimes located near the towns Entre Rios (SC) and Quaraí (RS). To characterize these materials analyses have been made by ICP, NAA, electron microscopy, water loss techniques and UV-VIS and NIR-FTIR spectroscopic measurements. Silanol complexes are found, which by radiation due to gamma rays form the color center NBOHC (Non-Bonding Oxygen Hole Center), showing absorption between 590 to 620 nm and leaving a transmission window at about 550nm, responsible for the green color. The spectroscopic water determination showed less molecular water (up to 2300 ppm by weight), probably due to remaining silanol complexes. The water content with up to 3200 ppm by weight exceeds the amount of charge balancing cations (Fe, Al, Li).

1. INTRODUCTION

In the last decades the use of quite strong ⁶⁰Co gamma radiation has shown very good results of color modification for quartz. Silica, in his stable form of quartz, a widespread mineral, has mainly two gem varieties, amethyst with his violet and citrine with his yellowish brown shades of color. But since a few years, other varieties appeared on the market like the “Green gold” or “Lima quartz”, the “Champagne” or “Beer” colored, the green colored variety called “Prasiolite” and the blue to blue-violet quartz called “Safirita or Blueberry Quartz” [1].

Quartz used for these treatments is mainly found in Brazil in two geological occurrences, the hydrothermal deposits of the basaltic rocks of the Paraná Basin and the veins in the quartzitic Serra do Espinhaço Range beside the deposits of the long Pegmatitic Belt, tied strongly to granitic rocks and of igneous origin. The hydrothermal quartz contain all the varieties of silica found in fractures and geodes of the basaltic rocks of the huge Parana

Basin and includes agates, amethyst, chalcedonies and the types which will show a green color after irradiation, as well as the silica varieties hosted by the vein systems of the quartzites of the Espinhaço Mountain Range.

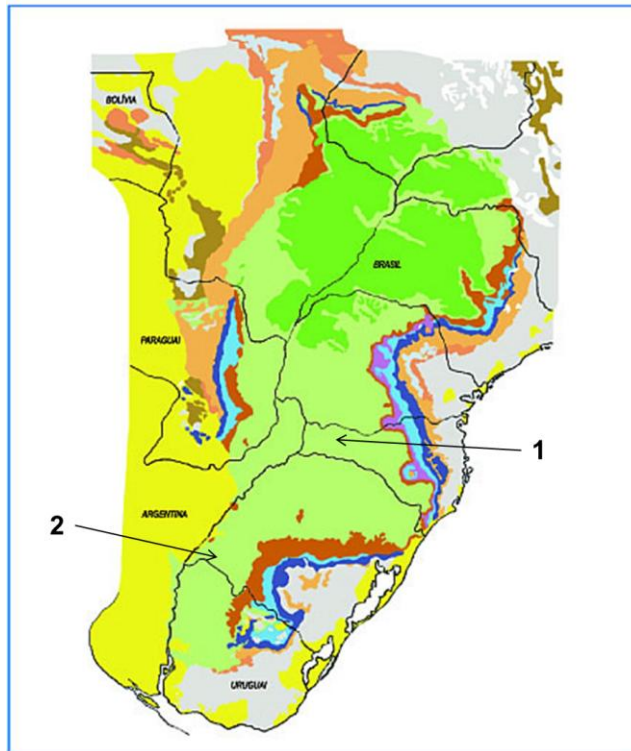
The mechanism of formation of green quartz found in nature or induced artificially by gamma radiation is very different from the ones widely discussed in the literature and responsible for the formation of the fumée, citrine and amethyst types of quartz, including the prasiolite (leak green quartz) formed by heating amethyst from Montezuma, Brazil. Two occurrences are known today, where this type of quartz can be found: Canada, at the Thunder Bay Amethyst Mine [2] , Ontario, a small district, and Brazil, at widely scattered geode occurrences along a 600 km stretch from Quaraí at Brazils southernmost tip to Uberlandia in Minas Gerais. These two occurrences have been formed by strong hydrothermal activities, at Thunder Bay due to tectonics and in Brazil by meteoric and hydrothermal waters of the Guarani aquifer. Some studies on irradiated green quartz from regions of Rio Grande do Sul were presented by Schultz-Güttler et al. [3,4], Henn & Schultz-Güttler [5] and Clerice [6] .

Quartz crystals formed by the processes mentioned above showed a very fast growth history facilitating the formation of growth defects (twinning, small angle tilting, mosaic growth, striations) [7,8,9] and the uptake of water in form of micro inclusions, molecular water, silanol (Si-OH) [9] and hydroxyl (OH). There is no correlation between water content and cations as in other color varieties. Instead, silanol complexes are formed, which by radiation due to gamma rays form the color center NBOHC (Non-Bonding Oxygen Hole Center), responsible for the green color [10].

2. MATERIALS AND METHODS

2.1. Materials

The quartz crystals used in the present work, generally of euhedral shape or fragments of crystals, comes from hydrothermal regimes created by the intrusions of basaltic rocks in the Parana Basin, Southern Brazil, and is derived from geodes or veins in rock fractures. The samples were collected in the regions of Entre Rios (SC) and Quaraí (RS) as shown in Fig.1.



1. Entre Rios (SC)
2. Quaraí (RS)

**Figure 1: Sampling regions of hydrothermal quartz from Entre Rios and Quaraí.
Adapted ABAS [11].**

2.2. Irradiation procedures

The batches of quartz were submitted to irradiation in the ^{60}Co Multipurpose Irradiator (Fig. 2) at the Radiation Technology Center (CTR), IPEN-CNEN/SP [12]. The samples were inserted into the irradiation devices built with screen of fine mesh of stainless steel fixed at structures made of the same material. These were then lowered to the base of the source storage pool of the irradiator that contains 51 sources of ^{60}Co producing a total of irradiation at about 205000 Ci or 7.58 PBq (August 2017).



Figure 2: Multipurpose Irradiator of the Radiation Technology Center from IPEN-CNEN/SP.

The total dose of gamma radiation applied to these batches is variable. Maximum doses applied were up to 450 kGy and dose rate 20 kGy/h. The particular dose of each batch was calculated as function of hours of irradiation to which the quartz was submitted, and the dose rate obtained through the reading of the dosimeters " Red Perpex 4034 " and of the dosimeters of cellulose triacetate (CTA) with triphenyl phosphate used in all runs positioned inside of the devices.

2.3. Methods of characterization

Some representative quartz crystals have been selected for preliminary chemical and spectroscopic characterization. The chemical composition has been analyzed by standard methods of ICP-Mass-Spectroscopy (Elan-6100DRC, Perkin Elmer) at the Chemical Laboratory of the Geosciences Institute, USP, by ICP-AES and NAA at NNA-Laboratory of the IPEN-CNEN/SP. Ultraviolet-Visible and Near Infrared (UV/VIS-NIR) spectroscopy from 200 to 3000 nm was done by use of the CARYSCAN 500 spectrometer at the Ionic Crystal Laboratory of the Physics Department, USP .And FTIR Perkin Elmer Universal ATR equipment with Sampling Accessory Spectrum 100 has been used to acquire the spectra of powdered material.

The determination of the concentration of total H₂O present in quartz was made using the technique of Loss of Ignition analysis. Scanning electron microscopy MEV located at IPEN has been used for information about the texture and topography of the samples mainly regarding Brazil Law twinning and the analyses of striations .

To examine the defects of growth or "Realbau" of samples of quartz, with regard to twinning, the polariscope and horizontal gemological research microscope , installed on Gemological Laboratory of the Institute of Geosciences of the University of São Paulo were used. The minimum dose necessary to obtain the green colour has been found by tests of saturation point in clear and transparent quartz samples by varying the doses. The samples were analyzed using the UV-VIS spectrophotometer Shimadzu LDPI of the laboratory of CTR-IPEN.

To study the stability of color to ultraviolet radiation exposure a process of accelerated exposure using an accelerated aging Chamber has been devised. This camera is EQUILAM, model EQUV that is installed in the Center of Science and Technology of Materials of the IPEN-CNEN/SP. It has 8 mercury fluorescent lamps of 40 Watts each that emit ultraviolet radiation in the UVA region of 340 nm.

3. RESULTS AND DISCUSSION

3.1. Chemical analysis

Chemical analysis ICP-OES and NAA in quartz samples of hydrothermal origin of Quaraí and Entre Rios are listed in Tables 1 and 2 and show a predominance of impurities of Fe, Al, Na, K and Ca.

Table 1: Optical emission spectrometry with argon plasma (ICP-OES)

<i>Element</i>	<i>Locality</i>	
	<i>Entre Rios (SC)</i>	<i>Quaraí (RS)</i>
Na	84 ± 4	109 ± 12
Al	158 ± 3	148 ± 2
K	77 ± 3	81 ± 2
Ca	< 2.0	< 2.0
Fe	211 ± 12	80 ± 1
Cr	< 8.0	< 8.0
Mn	< 1.5	< 1.5
Zn	< 5.0	< 5.0
Ni	< 16.0	< 16.0
Cu	< 25.0	< 25.0
Ba	< 3.0	< 3.0
Mg	< 1.5	< 1.5

Table 2: Neutron Activation Analysis – NAA

<i>Element</i>	<i>Locality</i>	
	<i>Entre Rios (SC)</i>	<i>Quaraí (RS)</i>
Cr	5.5 ± 0.9	1.17 ± 0.13
Fe	124 ± 18	19.44 ± 0.15
K	39 ± 2	49 ± 12
Mn	0.7 ± 0.1	4.6 ± 0.3
Na	53 ± 4	80.2 ± 3.1
Zn	nd	1.98 ± 0.43
As	16 ± 3	22 ± 2
Co	69 ± 2	487 ± 4
Ce	133 ± 7	65 ± 11
La	9 ± 1	32 ± 9
Sb	33 ± 6	92 ± 7
Sm	1.7 ± 0.5	2.7 ± 0.3
Sc	1.5 ± 0.5	0.68 ± 0.03
Th	nd	486 ± 11

A comparison of the ranges of concentrations of trace elements, shown in Tables 1 and 2 with data of quartz samples from various localities of Brazil presented by work of Iwasaki et al. [13] shows that the chemical composition of samples of all these regions is very similar, and the variations shown are typical features of both the geological environment of formation, as well as local conditions and the time of each crystal growth.

3.2. FTIR and ATR Spectroscopy

The graph, shown in Fig.3, obtained by FTIR spectrometry of quartz samples of Quaraí/Artigas shows strong absorptions of H₂O and Si-OH respectively near the regions of 5300 cm⁻¹ and 4500 cm⁻¹ after Fukuda et al. [14]. These concentrations can be related to the presence of polysynthetic twinning of Brazil Law [15] facilitating the capture of OH groups and water.

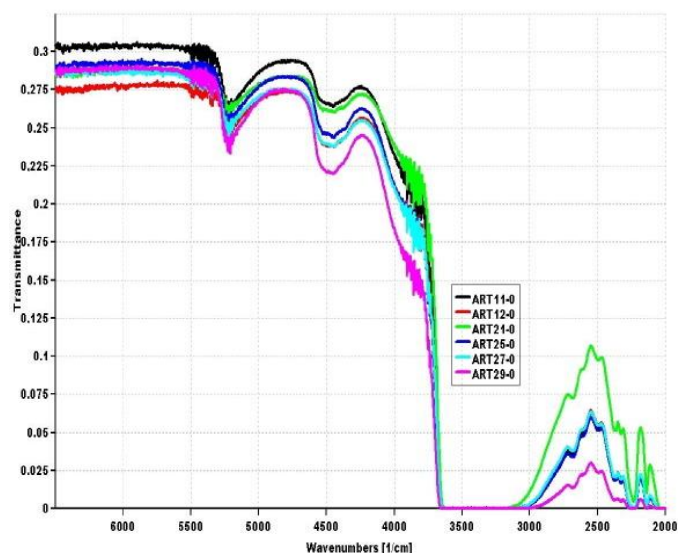


Figure 3: FTIR spectra of samples in the area of molecular H₂O at around 5300 cm⁻¹ and SiOH at around 4500 cm⁻¹.

The interpretation of spectra obtained by ATR spectroscopy and presented in Fig. 4 was very limited since it was not possible to analyze the number of secondary peaks by deconvolution of the main peak. The peaks of the SiO₄ tetrahedron's vibration found in the ATR spectrum corresponds well to values cited in the literature [2] a spectrum with a peak around 1070 cm⁻¹, two symmetrical peaks between 750 and 800 cm⁻¹ and a little "shoulder" around 1200 cm⁻¹. The sample is from an outcropping near the town of Entre Rios and judging from symmetry and the narrow bands it is considered a good quartz crystal. The superposition of peaks in the spectra and the limitation of the technique in the deconvolution of curves did not allow more discussion in this work only a few results obtained are shown.

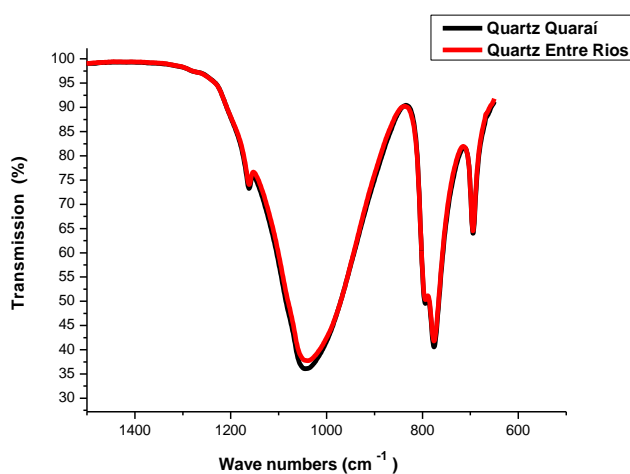


Figure 4: Infrared ATR spectroscopy of Quaraí and Entre Rios quartz samples.

3.3. Analysis of growth defects by use of the Polariscope and Gemological Microscope

Quartz crystals of the Quaraí region were analyzed with polarized light and, growth defects in the samples have been found. The 24 polished slices were the same ones used in FTIR infrared spectroscopy. This analysis shows that the samples from hydrothermal regions feature Brazil Law twinning as shown by Fig. 5 (a) and (b) .

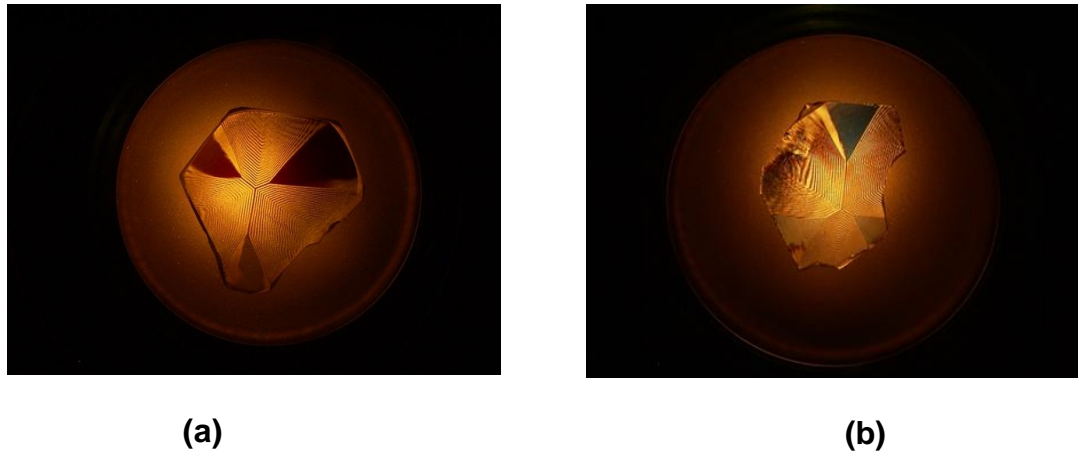


Figure 5: Images obtained in the polariscope in quartz plates of the Quaraí (a) and (b) with Brazil Law twinning.

This is a twinning called polysynthetic whereby the crystal is composed of thousands of crystalline planes (thin slices) with nano-sized micrometric thickness, interconnected and interwoven with numerous planar defects giving rise to oxygens without connection with other tetrahedra. This state is ideal for forming Silanol (Si-OH) and NBO (Non-Bridging Oxygen or Non-Bonding Oxygen), forming the NBOHC color centers, responsible for the green color [10].

3.4. Measurements of radiation dose for color saturation

These measurements were made preliminary to detect the limit of radiation dose. In the first series small chips of 1 cm thick were selected. In the second all chips from the region of Quaraí have been selected. These samples were irradiated with doses of 10, 30, 50, 70, 90 and 110 kGy, and the greenish color with light gray tint has been obtained. Another group of quartz samples was irradiated with the same doses and produced green quartz with strong grey color component. The absorbance coefficient α was calculated using the equation:

$$\alpha = (A - A_{\text{base}}) / d \quad \text{where:} \quad (1)$$

α = linear coefficient (cm^{-1})

A – A base = difference absorbance of the sample and the baseline, supposedly linear

d = thickness of the plate or the average thickness of quartz crystal.

Fig. 6 shows the graph of absorbance (cm^{-1}) at around 620 nm as a function of radiation dose (kGy) for samples of the same thickness. One notes the increase of absorbance value and consequently of green tone at a more or less constant rate but slowing down above 90 kGy irradiation. The same result was obtained from a group of green quartz with radiation doses reaching 2000 kGy [16]. Once again, the values of absorbance above 90 kGy radiation dose showed no increase. It appears that there is a specific concentration of water and hydroxyl and the formation of color centers is limited. Irradiation with higher doses do not produce more intense colors. The absorbance spectra of quartz samples irradiated are shown in Fig. 7, 8 and 9.

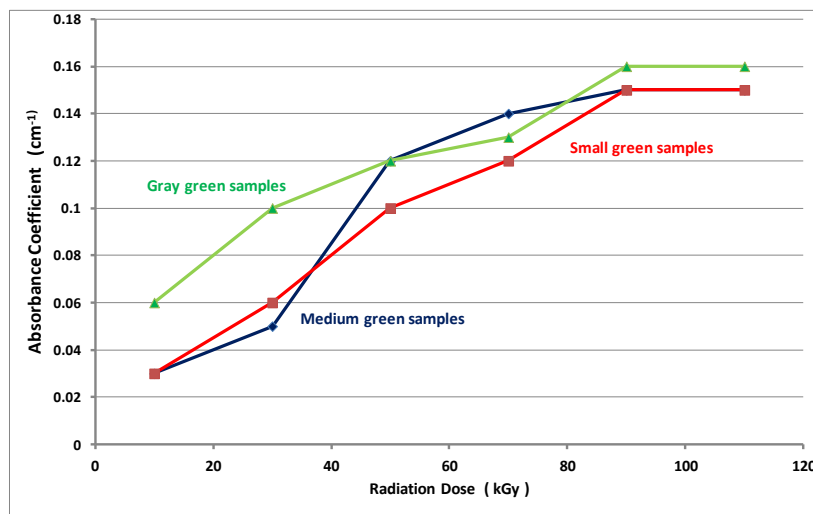


Figure 6: Absorbance at 620 nm (cm^{-1}) as a function of radiation dose (kGy) for small and medium samples of green and gray green quartz of Quaraí region.

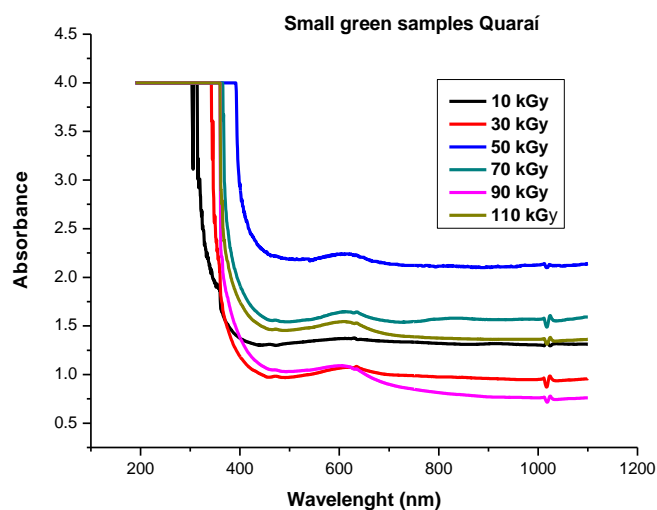


Figure 7: Qualitative absorbance spectra of small quartz pieces irradiated at various doses.

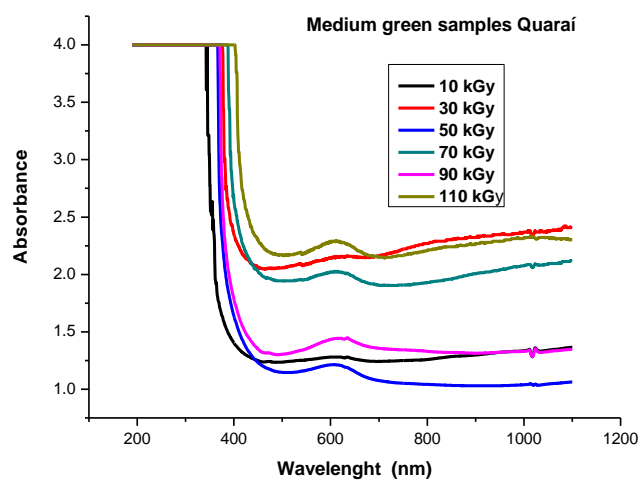


Figure 8: Qualitative absorbance spectra of medium quartz pieces irradiated at various doses.

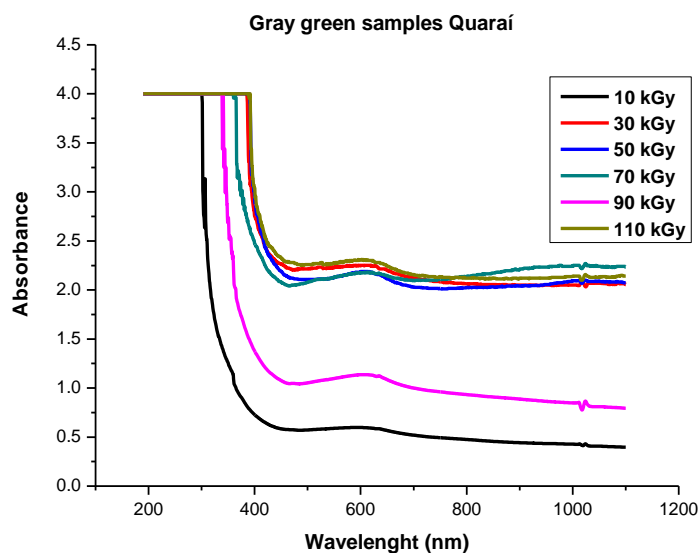


Figure 9: Qualitative absorbance spectra of gray green quartz pieces irradiated at various doses.

3.5. Color stability by UV radiation

To analyze the loss of color with time of exposure to ultraviolet radiation, irradiated green quartz samples of the Quaraí region were placed in an aging test chamber with radiation-emitting ultraviolet lamps in the UVA region of 340 nm. In this assay the samples of quartz clear green, dark green and medium were exposed to UV radiation by 1440 hours, approximately 60 days. After this period a decrease in the intensity of the green color as shown in Fig. 10 and 11 can be observed and also by the spectra obtained by UV-VIS spectroscopy analysis shown in Fig. 12 and 13. For comparison with data shown above Table 3 shows the calculated absorbance coefficients α of these samples.

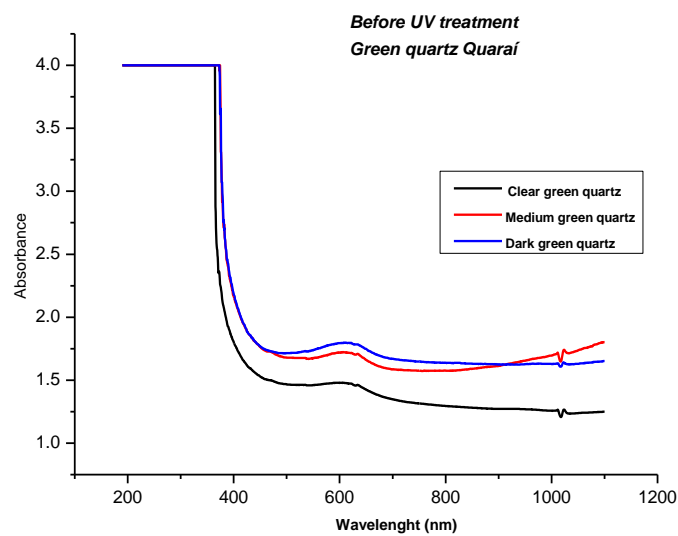


Figure 10: Qualitative absorbance spectra of green quartz Quaraí before UV radiation treatment.

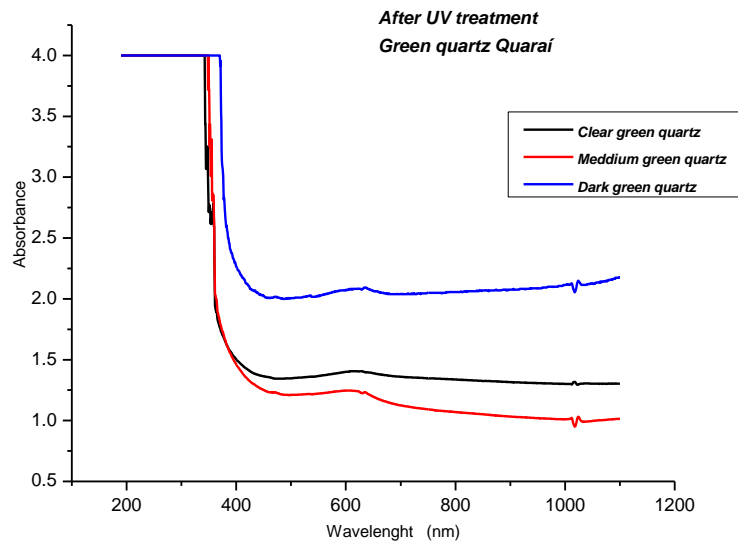


Figure 11: Qualitative absorbance spectra of green quartz Quaraí after UV radiation treatment.



Figure 12: Clear, medium and dark green quartz Quaraí before UV treatment



Figure 13: Clear, medium and dark green quartz Quaraí after UV treatment

TABLE 3: Absorbance coefficient (α) of green quartz samples, before and after UV radiation treatment

<i>Occurrences</i>	<i>Absorbance coefficient (α) (cm^{-1})</i>					
	<i>Before UV</i>			<i>After UV</i>		
	<i>Dark Green</i>	<i>Meddium green</i>	<i>Clear green</i>	<i>Dark green</i>	<i>Meddium green</i>	<i>Clear green</i>
Quaraí	0.13	0.11	0.10	0.08	0.10	0.08

It may be noted in the spectra obtained after UV treatment of 1440 hours, that the absorbance coefficients (cm^{-1}) from samples before exposure to UV radiation are relatively larger than the coefficients of the samples after exposure, indicating that there was loss of intensity of the green color.

4. CONCLUSIONS

It could be shown that natural quartz develops by gamma irradiation a color center producing green colors in samples. The reasons for this are linked to hydrothermal environments in which occurs a very fast growth of crystals with multiple defects formation (Brazil Law twinning) facilitating the incorporation of high concentrations of hydroxyl and water thus forming silanol (Si-OH). These high concentrations of molecular water and silanol can be seen in spectra by FTIR spectrometry carried out on samples of Quaraí and Entre Rios by strong absorptions close to 5300 cm^{-1} and 4500 cm^{-1} . Analyses with the polariscope and gemological microscope on samples of quartz of the Quaraí area show high amounts of near-perfect Brazil Law twinning, which involves the whole crystal.

The tests performed on the samples of Quaraí for determining the radiation limit of dose for green color saturation showed approximately 90 kGy as dose at which occurs green color saturation. This fact indicates that in quartz crystals there is a specific concentration of molecular water and hydroxyl and the formation of color center is limited by this. The radiation with higher doses will not produce more intense colors.

The tests performed to study the stability of the colour by exposure to ultraviolet radiation in the UVA region (60 days), showed that the coefficients of absorbance of samples before exposure to UV radiation are relatively larger than the coefficients after treatment, indicating that there was approximately 10 to 50 % of loss of intensity of the green color. This fact has to be considered by using these green quartz samples as gemstones in the trade. The intensity of green color obtained by the same dose depends on the amount of silanol (Si-OH) and hydroxyl (OH) incorporated in quartz crystals.

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