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Studies of Hydrothermal Quartz from Ametista do Sul Treated with Gamma Radiation

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1. Introduction

The hydrothermal quartz from Ametista do Sul is found in intrusions of basaltic rocks of the Paraná Basin which have been formed by strong hydrothermal activities. That way much quartz crystals showed a very fast growth history faciliting the formation of growth defects (twinning, small angle tilting, mosaic growth, striations) [1,2,3] with the simultaneous uptake of water in form of molecular water, silanol (Si-OH) [3] and hydroxyl (OH). In hydrothermal quartz of Ametista do Sul, this content of molecular and silanol is responsible for the formation of NBOHC (Non-Bonding Oxygen Hole Center) defects that produce, by gamma radiation, the green color [4].
Studies on hydrothermal green quartz, from some regions of the Paraná Basin, were presented by Henn & Schultz-Güttler [5], Schultz-Güttler et al. [6,7] and Enokihara [8].

2. Methodology

Representative samples of quartz crystals were selected for chemical and spectroscopic characterization. For the chemical analysis, the techniques of Optical Emission Spectrometry, with Argon Plasma (ICP-OES), at the Chemical Laboratory and of Neutron Activation Analysis, at the NAA Laboratory, both from IPEN-CNEN/SP, have been used.
The FTIR Spectroscopy were made by using the FTLA 2000 – ABB Bomem Spectrometer, at the Radiopharmacy Center of IPEN-CNEN/SP.
The technique of Loss of Ignition Analysis (LOI) was conducted to determine the total H_2O concentration present in the samples of colorless and green color quartz , and to check a possible correlation of color with the concentration of water.
To examine the defects of quartz samples growth, with regard to twinning, the Polariscope and Gemological research Microscope, installed at the Gemological Laboratory of the Institute of Geosciences of the University of São Paulo, were used.
To analyze the loss of color as to time of exposure to ultraviolet radiation, an EQUILAM chamber, model EQUV that is installed in the Materials Technology Center of the IPEN-CNEN/SP, was used. It has 8 mercury fluorescent lamps of 40 Watts each, emitting ultra-violet radiation of 340 nm, in the UVA region. The samples were analyzed using the UV-VIS spectrophotometer Shimadzu LDPI, from the CTR-IPEN laboratory.
For the tests of color stability by heating, a Black & Decker electric furnace with maximum temperature up to 350 ºC and glass cover, allowing visual monitoring of the discoloration of the quartz samples, was used.

3. Results and Discussion

The graph, shown in Fig.1, obtained by FTIR spectrometry of quartz samples of Ametista do Sul shows strong absorptions of H_2O and Si-OH respectively near the regions of 5300 cm^{-1} and 4500 cm^{-1} after Fukuda et al. [9]. These absorptions are related to the NBOHC defects and are very different from the color centers originated by the replacements by impurities of Fe Si and Li. NBOHC are defects in the crystal structures along dislocations without any direct connection with the tetrahedra of SiO_4 or may be present in the regions of bonds highly strained as for instance the twinning in step growth in spiral growth defects [1,2]. Examining the green quartz crystals by higher magnification one can find fine striations parallel to romboedrical faces that are called Brazil Law twinning [10].

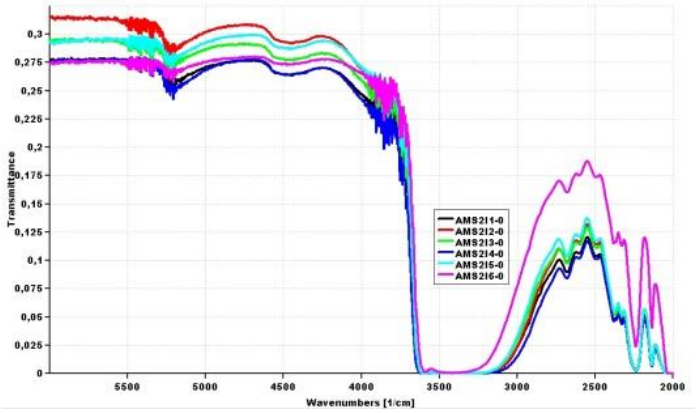

Figure 1: FTIR spectra of samples in the area of molecular H_2O at around 5300 cm^{-1} and SiOH at around 4500 cm^{-1}.

The analyzes made with Polariscope and Gemological Microscope presented in Figs. 2 (a) and (b) show the samples with perfect Brazil Law twinning involving the whole crystal. This twinning is called polysynthetic, with crystal composed of thousands of crystalline planes (thin slices), with nano-sized micrometric thickness, interconnected and interwoven with numerous planar defects and giving rise to oxygen without connection with other tetrahedra. This state is ideal for forming Silanol (Si-OH) and NBO (Non-Bridging Oxygen or Non-Bonding Oxygen), producing the NBOHC color centers, responsible for the green color [4].

(a) **(b)**

Figure 2: Images obtained in the polariscope in quartz plates of the Ametista do Sul (a) and (b) with Brazil Law twinning.

The results of chemical analysis carried out by ICP-OES and NAA indicate that the chemistry of quartz samples of hydrothermal origin, from Ametista do Sul , are dominated mainly by impurities of Fe (89-142 ppm), Al (287 ppm), Na (195-258 ppm), K (104-91 ppm) and H_2O, all of them determined in the Fire Loss Analysis (LOI). The results of the samples analyzed are shown in Table I. As it has been shown by Ihinger et al. [11], the concentrations of trace elements and water vary as a function of certain growth sectors and directions. It was noticed that the growth rate of crystals affects, strongly, the incorporation of trace elements.

Table I: Optical emission spectrometry with argon plasma (ICP-OES) and Neutron Activation Analysis – NAA

Element **(µg/g)**	***Analysis***	
	ICP-OES	***NAA***
Na	195 ± 6	258 ±20
Al	287 ± 1	-
K	104 ± 2	91 ± 9
Ca	50 ± 7	-
Fe	89 ± 14	142 ± 38
Cr	< 8,0	21,1 ± 2,9
Mn	< 1,5	1,1 ± 0,2
Zn	< 5,0	1,6 ± 0,1

The Fire Loss Analysis (LOI) conducted in the samples of colorless and green color quartz from Ametista do Sul shows a clear relationship between the amount of water and the resulting color of irradiation. Analyzing the water values presented in Table II, one notes that the variation of these values accompanies well the intensity of the green color. The fact that the same shades of colour contains different amounts of water determined by the LOI, may indicate that a part of water can still be retained in the samples in form of Si-OH.

Table II : H_2O concentration (ppm) in quartz samples determined by Loss of Ignition Analysis (LOI) and correlation with color.

Locality	***Dark green***	***Clear green***	***Colorless***
Ametista do Sul	1697	1284	182

In the assay of the stability of color to ultraviolet radiation, clear green, dark green and medium samples of quartz from Ametista do Sul were exposed to UV radiation by 1440 hours, approximately 60 days. After this period may be calculated the absorbance coefficient α of these samples shown in Table III .

Table III : Absorbance coefficient (α) of green quartz samples, before and after UV radiation treatment.

Occurrences	*Absorbance coefficient (α) (cm^{-1})*					
	Before UV			*After UV*		
	Dark green	*Medium green*	*Clear green*	*Dark green*	*Medium green*	*Clear green*
Ametista do Sul	0,09	0,09	0,09	0,07	0,07	0,07

The experiments of color loss due to heating performed in the samples of green quartz, from Ametista do Sul region, irradiated up to 300 kGy, are given in Table IV. This Table IV shows the times that the samples, divided into groups of 1 to 6, according to the shade of green, varying from dark to clear, led to lose color totally, at temperatures of 150 °C, 175 °C, 200 °C , 225 °C and 250 °C.

Table IV : Time for total discoloration of the green quartz samples from the Artigas region**.**

Temperature (ºC)	*Time for total discoloration (min)*					
	Group 1	*Group 2*	*Group 3*	*Group 4*	*Group 5*	*Group 6*
150	49	42	39	40	31	32
175	42	35	32	33	25	23
200	24	22	21	20	15	13
225	19	17	18	16	12	12
250	16	12	13	13	11	10

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 Ametista do Sul by strong absorptions close to 5300 cm^{-1} and 4500 cm^{-1} which by irradiation with gamma rays produce the so called Nonbonding Hydroxyl Defect, NBOHC. Analyses with the Polariscope and Gemological Microscope on samples of quartz of the Ametista do Sul area show high amounts of near-perfect Brazil Law twinning, which involves the whole crystal.

It could be observed by the analysis of Loss of Ignition (LOI) the correlation between the water concentration and the intensity of the green color (dark to clear), showing that the greater the amount of water, the higher the intensity of green color after irradiation.

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