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Comparative analysis of quartz treated with gamma radiation originated from the hydrothermal geodes of the Paraná Basin, with quartz generated in the hydrothermal veins of Serra do Espinhaço.

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ABSTRACT

In Brazil, hydrothermal quartz may be found in the geodes of the basaltic rocks of the Paraná Basin and in the vein systems of quartzites of the Serra do Espinhaço. The quartz of hydrothermal origin of the Paraná Basin contains a great amount of structurally bound water in the form of molecular water, silanol, hydroxyl and abundant growth defects that are responsible for the green color formed by irradiation. To register the influence of water in the formation of the green color in the quartz of the Paraná Basin, quartz samples from the following regions were analyzed: Artigas, located in the Paraná Basin, Curvelo and Brejinho located in Serra do Espinhaço. The quartz from Artigas, formed at low temperature, has high concentration of molecular water and silanol and a greater amount of Fe than Al. The quartz from Curvelo with Al, but, without water molecular and

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silanol was formed by intermediate temperature and the quartz from Brejinho has very little Al, Fe and a small silanol and molecular water content. To characterize these samples, ICP, NAA, and NIR-FTIR spectroscopic measurements have been taken together with water loss techniques. The analysis by FTIR spectrometry of Artigas quartz samples shows strong absorptions of H_2O and Si-OH, respectively, near the regions of 5300 cm^{-1} and 4500 cm^{-1}. This content of molecular water and silanol in hydrothermal quartz of Artigas is responsible for the formation of NBOHC defects that produce, by gamma radiation, the green color.

***Keywords*: Quartz irradiation, quartz enhancement, gemstones treatment.**

1. INTRODUCTION

Several minerals, mainly quartz, are treated worldwide in many irradiation centers and they use this technique to activate the so-called "color centers" in minerals and produce higher valued gemstones. The presence of defects and faulty structures in the minerals, combined with the effect of the ionizing radiation, produces changes in the optical properties of these materials. These alterations are manifested as color.

In Brazil, hydrothermal quartz may be found in the Paraná Basin and in the Serra do Espinhaço Range. The hydrothermal quartz contains all the varieties of silica found in fractures and geodes of the basaltic rocks of the huge Parana Basin, including agates, amethyst, chalcedonies and the types which will show green color after irradiation, as well as the silica varieties hosted by the vein systems of the quartzites of the Espinhaço Mountain Range.

The formation of the green quartz found in nature or induced artificially by gamma radiation is very different from that 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. Schultz-Güttler [1] and Henn & Schultz-Güttler [2] did some considerations regarding the definitions of Prasiolite and Green quartz.

Two occurrences of green quartz of hydrothermal origin have been located in the region of the Paraná Basin, in Brazil and Uruguay, and in Thunder Bay Mine, in Canada, as described by Hebert & Rossman [3]. These two occurrences were formed under strong hydrothermal activity; the one of Thunder Bay is due to tectonism and that of the Paraná Basin is related to the activities of meteoric water and hydro-thermal events of the Guarani aquifer. These hydrothermal quartz crystals have a history of very fast growth, allowing the formation of abundant growth defects, such as twinning, mosaic formation with small inclined angles and striations [4,5,6], facilitating the absorption of water in the form of molecular water, silanol (Si-OH) [6], hydroxyl (OH) and as micro inclusions. This content of molecular water and silanol in hydrothermal quartz from the Artigas is responsible for the formation of NBOHC defects that produce, by gamma radiation, the green color [7].

The green quartz from hydrothermal origin may be found at widely scattered geode occurrences, along a 600 km stretch from Quaraí (Brazil) and Artigas (Uruguai) to Uberlandia in Minas Gerais.

Some studies on irradiated green quartz, from some regions of Rio Grande do Sul, were presented by Henn & Schultz-Güttler [2], Schultz-Güttler et al. [8, 9] and Enokihara [10].

2. MATERIALS AND METHODS

Representative samples of quartz crystals were selected for chemical and spectroscopic characterization. The samples used were hydrothermal origin macrocrystalline colorless quartz, with the shape of plates, chips, powder and faceted crystals. These samples are from the hydrothermal geodes of the Paraná Basin and were collected in the locality of Artigas (Uruguai). Samples of quartz, also, from hydrothermal veins of Serra do Espinhaço located in the regions of Brejinho (BA) and Curvelo (MG.), were used as reference materials and for comparison purposes .

2.1. Irradiation procedures

The irradiation of colorless quartz samples were made in the ^{60}Co Multipurpose Irradiator, installed at the Radiation Technology Center of IPEN-CNEN/SP. It is a multipurpose compact type radiator, containing, currently, 64 pencils of $^{\mathbf{60}}$Co set in magazines. The quartz samples, enclosed in wired containers, were irradiated under water to maintain a low temperature. Maximum doses applied were up to 450 kGy. These doses were determined through the reading of dosimeters of polymethyl methacrylate (PMMA), Red Perspex 4034 type, and dosimeters of cellulose triacetate (CTA), with triphenyl phosphate.

2.2. Methods of characterization

Various techniques of chemical analysis and spectroscopy were employed to characterize the samples of quartz. 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.

To document the influence of water on the green color formation, analyses by FTIR spectroscopy were performed using the FTLA 2000 – ABB Bomem spectrometer, at the Radiopharmacy Center of IPEN-CNEN/SP.

The determination of total H_2O concentration, present in quartz, was accomplished using the technique of Loss of Ignition Analysis.

To examine the defects of quartz samples growth, with regard to twinning, the polariscope and horizontal gemological research microscope, installed at the Gemological Laboratory of the Institute of Geosciences of the University of São Paulo, were used.

3. RESULTS AND DISCUSSION

3.1. Chemical analysis

Chemical analysis ICP-OES and NAA were carried out in quartz samples from hydrothermal origin of Artigas and are listed in Table 1, showing a predominance of Al, Fe, Na and K impurities.

The results of chemical analysis carried out by ICP-OES and NAA indicate that the chemistry of quartz samples of hydrothermal origin, from Artigas, are dominated mainly by impurities of Fe (159-128 ppm), Al (286 ppm), Na (147-156 ppm) and H_2O.

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

Element (µg/g)	Analysis	
	ICP-OES	NAA
Na	147 ± 2	156 ± 11
Al	286 ± 19	-
Ca	< 2.0	-
Fe	159 ± 8	128 ± 37
Cr	< 8.0	8.7 ± 0.8
Mn	< 1.5	3.0 ± 0.2
Zn	< 5.0	nd
Ni	< 16.0	-
Cu	< 25.0	-
Ba	< 3.0	-
Mg	< 1.5	-
Co	-	91 ± 23
Ce	-	198 ± 64
Sb	-	18 ± 6
Sm	-	4.7 ± 0.6
Sc	-	0.81 ± 0.42

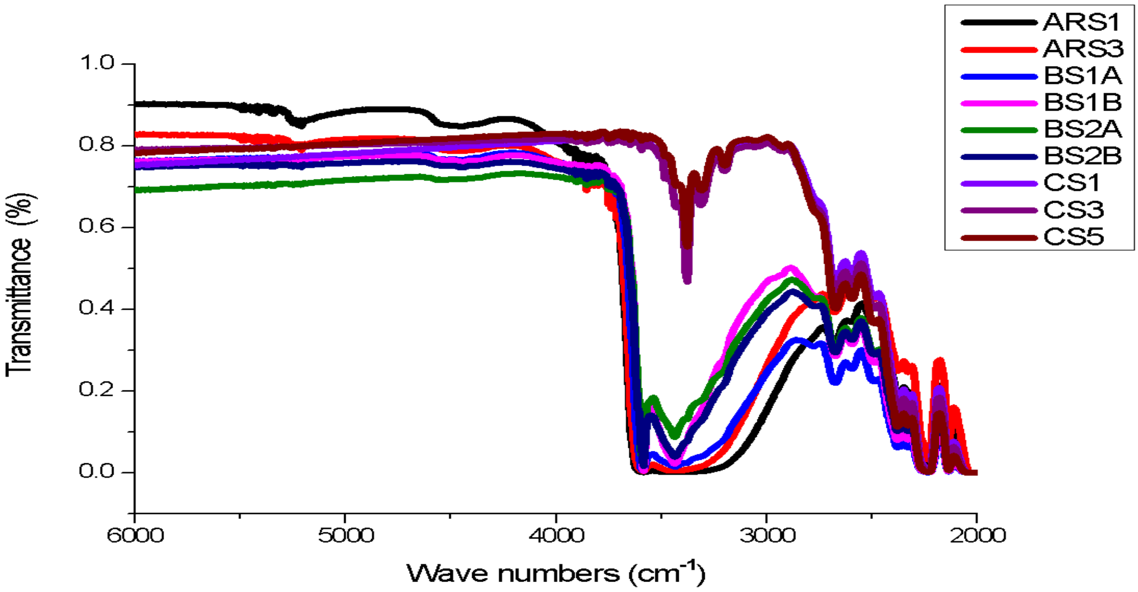
3.2. FTIR Spectroscopy

The graph, presented in Figure 1 shows the FTIR spectra of transmittance of the samples from Artigas (ARS), Brejinho (BS) and Curvelo (CS) regions. The graph shows the distribution of H_2O contents in various molecular forms in the samples.

Artigas samples show strong absorptions of H_2O and Si-OH, respectively, near the regions of 5300 cm^{-1} and 4500 cm^{-1} [12]. These concentrations may be related to the presence of polysynthetic twinning of Brazil Law [13], facilitating the capture of water and OH groups. Brejinho samples show larger absorption near 3400 cm^{-1}, indicating slightly higher molecular water content. Samples of Curvelo are poor in H_2O and show peaks linked to Al, Li and OH.

With respect to silanol (Si-OH), analyzing the range of the wave numbers near 4500 cm^{-1}, samples from Curvelo did not show any transmission, indicating the total absence of silanol. Brejinho samples showed a small absorption of silanol (4500 cm^{-1}), far lower than Artigas samples.

Figure 1: *FTIR spectra of quartz samples from Artigas, Brejinho and Curvelo regions*.



Source: The Authors

According to Lias et al. [14], the growth rate influences strongly on the incorporation of water and other impurities. In addition, some quartz sectors are better able to absorb impurities, as a function of temperature and speed of growth. This incorporation of water may take place in two different ways: as a molecule wholly fixed in the gaps, in the channels of the structure or in hydroxyl (OH) form. The analysis of infrared absorptions in the medium region, from 400 cm $^{-1}$ to 4000 cm $^{-1}$, does not allow these two forms to be distinguished

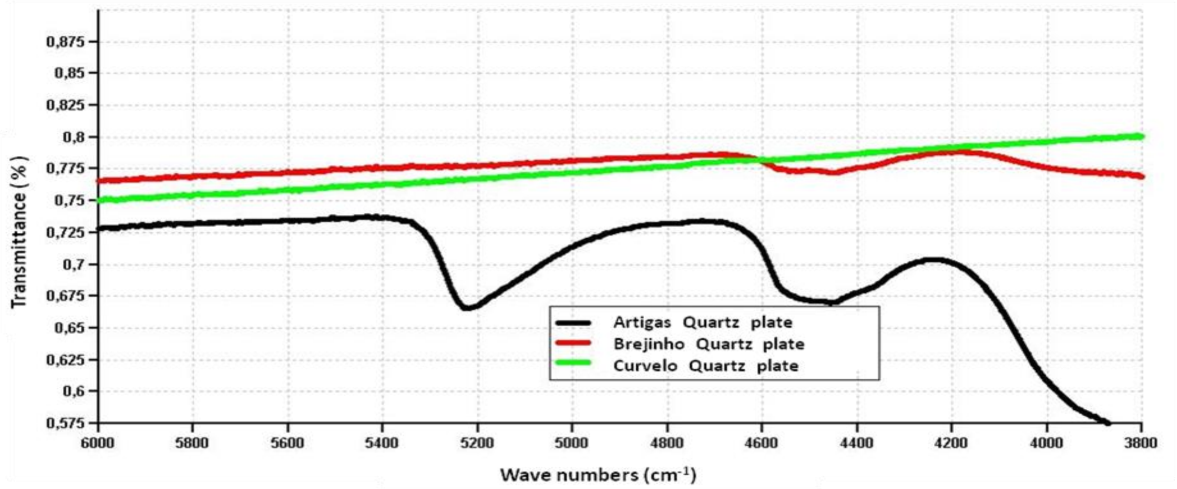
In previous works, especially by Kats [15], the OH bonds with trace elements such as Al and Fe are known, but not their specifications. These specifications may be studied only by absorption analysis in the near infrared between 4000 cm $^{-1}$ to 8000 cm $^{-1}$. In such case, larger thickness samples were necessary in order to have a higher absorption, as the intensities of a higher order of absorption are weaker.

To document this variable specification, samples from various sources were analyzed. A Curvelo (MG) crystal plate from a hydrothermal vein, originated by medium temperature and chemical composition determined by the presence of Al; a crystal plate from Brejinho (BA), with similar formation conditions, but, with the presence of both Al and Fe, and a crystal plate from Artigas (Uruguai), originated by low temperature conditions, derived from a hydrothermal geode and with the presence of Fe and Al.

In Figure 2, the transmittance spectra of these localities are shown, in the range of 6000 to 4000 cm^{-1}. It may be observed that the quartz plate from Curvelo shows, in this interval, a line without absorptions. The quartz plate from Brejinho shows absorptions between 4300 and 4600 cm^{-1}. Finally, Artigas quartz plate shows absorptions between 4300 - 4700 cm^{-1} and near 5200 cm^{-1}. The absorptions in the 4400 cm^{-1} range show ripples, indicating various absorption bands.

According to Aines et al. [16], the absorptions in the vicinity of 4400 cm^{-1} are related to T-OH, with T indicating tetrahedron. Hence, these absorptions may be Al-OH, as well as Si-OH (silanol). The absorption near 5200 cm^{-1} is related to molecular H_2O. Then, it may be concluded that the Curvelo sample contains little or no molecular water or silanol concentration. Brejinho sample contains little silanol concentration as well as little Brazil Law twinning and it has little or no amount of molecular water, while Artigas sample shows very well defined molecular water and silanol content.

Figure 2: *Spectrum in the near infrared range of quartz samples from Artigas, Brejinho and Curvelo regions, with various water specifications.*



Source: The Authors

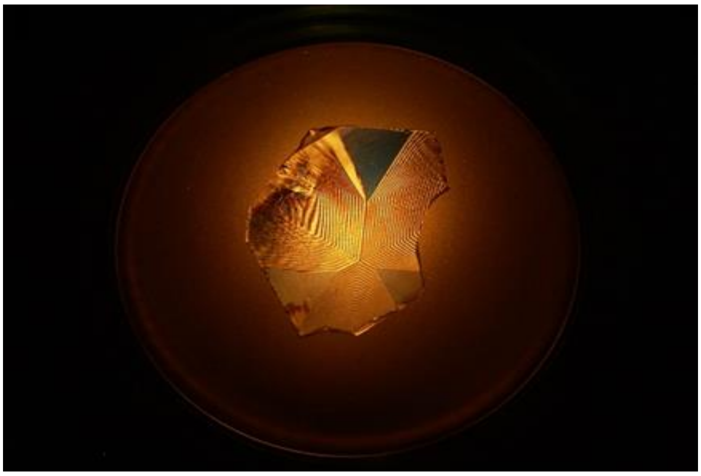
3.3. Analysis of growth defects by use of the Polariscope and Gemological Microscope

Analysis of growth defects with the Polariscope and Gemological Microscope were analyzed in the samples of Quaraí/Artigas, Brejinho e Curvelo regions. The polished slices were the same ones used in the FTIR infrared spectroscopy.

The quartz samples of Artigas region from the geodes of the Paraná Basin (low pressure and temperature conditions) are heavily twinned. This analysis shows that samples of Brejinho and Curvelo regions originated from hydrothermal regimes of Serra do Espinhaço (intermediate pressure and temperature) and present few traces or no Brazil Law twinning.

Figure. 3 shows the image obtained in the polariscope of a quartz plate from Quaraí/Artigas region 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 [7].

Figure 3: *Image of a quartz sample from Quaraí/Artigas region with Brazil Law twinning.*

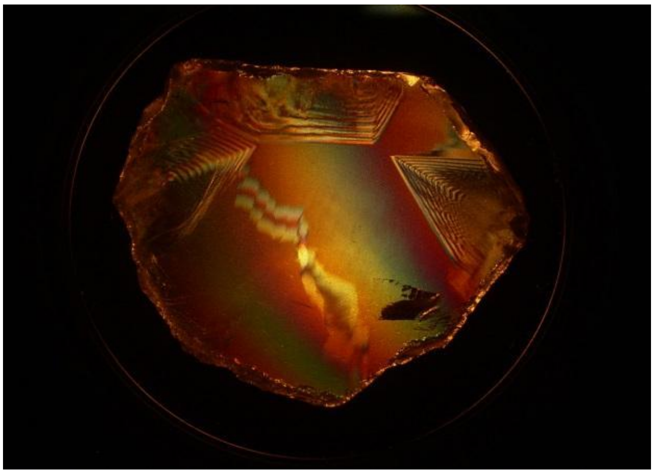


Source: The Authors

Figure 4 shows the image of a hydrothermal quartz plate from Brejinho region (Serra do Espinhaço), where there is a decrease in Brazil Law twinning.

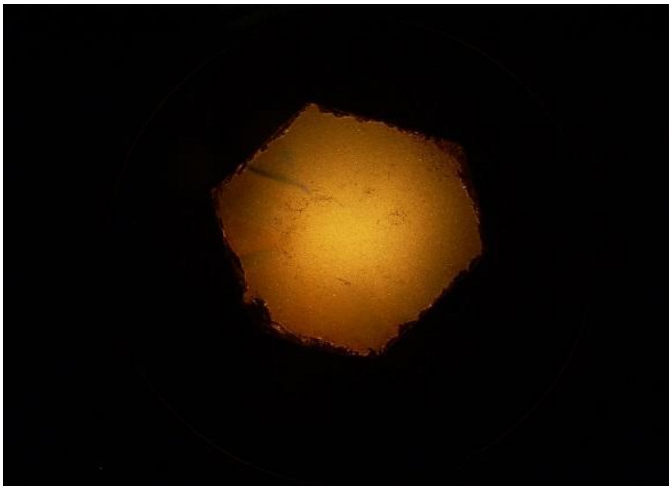
This fact does not occur with the hydrothermal quartz sample from the Curvelo locality (Serra do Espinhaço) presented in Figure 5, which does not show any Brazil Law twinning.

Figure 4: *Image of a quartz sample from Brejinho region.*



Source: The Authors

Figure 5: *Image of a quartz sample from Curvelo region.*



Source: The Authors

3.4. Loss of ignition (LOI) analysis

Loss of ignition analysis was performed to determine the concentration of total H_2O present in the samples of colorless and green color quartz from Artigas region, and to verify a possible correlation between the color and the concentration of water. The result presented in Table 2 shows a clear relationship between the amount of water and the consequential irradiation color.

Table 2: H_2O concentration (ppm) in quartz samples determined by Loss of ignition analysis (LOI) and the correlation with color.

Locality	Dark green	Clear green	Colorless
Artigas	963	665	173

From the data presented in Table 2, it may be noticed that the variation of these values accompanies the intensity of the green color. The fact that the same shades of color contain different amounts of water determined by LOI, could indicate that a part of the water may be still retained in the samples, in the form of Si-OH. To obtain more data on the amount of water, LOI analyses were performed in the laboratory of chemistry of the Institute of Geosciences of USP, as shown in Table 3. The content is given as a percentage and concentration (ppm) of water.

Table 3: H_2O quantity in percentage and ppm from Artigas region analyzed by Loss of ignition analysis (LOI).

Locality	% H_2O	Concentration H_2O (ppm)
Artigas	0.20	2000

The value presented in Table 3 is high. Therefore, with an amount of water far exceeding the contents of trace elements, as indicated previously, it is not possible to make similar correlations, as shown by Iwasaki et al. [17], between the water content and the sum of trace elements. The high concentration of water, whether in the form of OH or molecular water, compensates for any lack of correlation with structural elements (substitutional and interstitial).

The differences of concentrations observed in Tables 2 and 3, with analyses performed at IPEN and IG-USP, may be explained by the fact that different physical forms were used in two analyses. The values obtained and presented in the samples of Tables 2 and 3 were used in the form of small splinters, whereas in the analyses done at IG-USP, quartz powder samples were used.

4. CONCLUSION

The FTIR spectroscopy analyses performed on Artigas samples showed absorptions between 4300 cm^{-1} and 4700 cm^{-1}, connected to Si-OH. A strong absorption, near 5200 cm^{-1}, is related to molecular water. This content of molecular water and hydroxyl in hydrothermal quartz is unique and it is responsible for the formation of defects called NBOHC that produce, by natural or artificial radiation, the green color in crystals from hydrothermal origin. This high concentration of silanol may be related to the presence of Brazil Law twinning in samples of hydrothermal quartz, as it may be observed in the images obtained by Polariscope and Gemological Microscope.

Brejinho samples, with chemical composition determined by Al and Fe, show small absorption, between 4300 cm^{-1} and 4600 cm^{-1}**,** related to Si-OH. However, they present little or no molecular water. Some Brazil Law twinning have been confirmed by the "Realbau" analysis, in the Polariscope and Gemological Microscope.

Differentely from geodes quartz from Paraná Basin, the veins quartz from Curvelo, with chemical composition determined by Al, observed in the NIR spectra, showed a line without the presence of absorptions in the regions of 4500 cm^{-1} and 5200 cm^{-1}, indicating absence of Si-OH and molecular H_2O. The analyses of samples with the polariscope and microscope did not show any Brazil Law twinning. The color obtained after irradiation and heating is gray (fumée).

The high concentrations of water may be proven by the analysis of Loss of ignition (LOI) performed on samples of the hydrothermal quartz from the Paraná Basin, in Artigas region

(2000 ppm). It could, also, be observed by LOI analysis 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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REFERENCES

[1] SCHULTZ-GÜTTLER R.A. Safirita: o quartzo azul brasileiro . **Diamond News**, v. 6, p. 45-46 2006.

[2] HENN U.; SCHULTZ-GÜTTLER R.A. Color enhanced quartz and its identification green, violet-blue and yellow green quartz from Brasil . **Canadian Gemmologist**, v. 30, nº 2, p. 46-54 2009.

[3] HEBERT L.B.; G.ROSSMAN G. Greenish quartz from the Thunder Bay Amethyst Mine Panorama, Thunder Bay, Ontario, Canada, **Canadian Mineralogist**, v. 46, p. 61-74, 2008.

[4] HOSAKA M.; MIYATA T.; TAKI S. Observations of striations on hydrothermally-grown prism faces of quartz, **Journal of Crystal Growth**, v. 75, p. 473-80, 1986.

[5] STEVENS-KALDEFF M.A. Cathodoluminescence microcharacterization of point defects in α quartz, **Mineral. Mag.**, 73(4), p. 585-605, 2009.

[6] SALH R. Defect related luminescence in silicon dioxide network: a review, **Crystalline Silicon Properties and Uses. Basu**, S. (Ed), InTech Rijeka, Croatia, p. 135-172, 2011.

[7] DEPARIS O.; BLONDEL M. Influence of the cladding thickness on the evolution of the NBOHC band in optical fibers exposed to gamma radiations, **Journal of Non-Crystalline Solids** v. 216, p. 124-128, 1997.

[8] SCHULTZ-GÜTTLER R.A.; ENOKIHARA C.T.; RELA P.R. Gamma irradiation of quartz from Paraná Basin, South America, In**: INTERNATIONAL NUCLEAR ATLANTIC CONFERENCE** , 2007, Santos, SP. Associação Brasileira de Energia Nuclear (ABEN), 2007.

[9] SCHULTZ-GÜTTLER R.A.; ENOKIHARA C.T.; RELA P.R. Characterization of color centers in quartz induced by gamma irradiation, In: **INTERNATIONAL NUCLEAR ATLANTIC CONFERENCE**, 2009, Rio de Janeiro. Associação Brasileira de Energia Nuclear (ABEN), 2009.

[10] ENOKIHARA C.T. Estudo do quartzo verde de origem hidrotermal tratado com radiação gama", Tese de Doutorado**, Instituto de Pesquisas Energéticas e Nucleares – IPEN-CNEN/SP**, São Paulo, 166 p., 2013.

[11] IHINGER P.D., ZINK S.I. Determination of relative growth rates of natural quartz crystals, **Nature**, v. 404, p. 865-869, 2000.

[12] FUKUDA J.; YOKOYAMA T.; KIRINO Y. Characterization of the states and diffusivity of intergranular water in a chalcedonic quartz by high temperature in situ infrared spectroscopy, **Mineralogical Magazine**, v.73, p. 825-835, 2009.

[13] MCLAREN A.C.; PITKEHTLY D.R. The twinning microstructure and growth of amethyst quartz, **Phys.Chem.Min**., v. 8, p. 121-135, 1982.

[14] LIAS N.C, GRUDENSKY E.E., KOLB E.D., LAUDISE R.A. The growth of high Q quartz at high growth rates , **Journal of crystal growth,** v. 18, p. 1-6 , 1973.

[15] KATS A. Hydrogen in Alpha-Quartz, **Philips Res. Repts**., v.17, p. 148, 1962.

[16].AINES R.D., KIRBY S.H., ROSSMAN G.R. Hydrogen speciation in synthetic quartz, **Physics Chemistry of Minerals,** v.11, p. 204-21, 1984.

[17] IWASAKI F.; IWASAKI H. Impurity species in synthetic and Brazilian natural quartz, **Japanese Journal of Applied Physics**, v. 32, p. 893-907, 1993.