SPECTROSCOPIC STUDY OF ROSE QUARTZ FROM THE TABOA PEGMATITE (BORBOREMA PROVINCE, BRAZIL) IRRADIATED WITH HIGH GAMMA DOSES

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INTRODUCTION

The origin of rose color in massive quartz from granitic pegmatites has been considered in numerous studies but no ultimate consensus has established until now. Several authors associate the rose coloration to the presence of substitutional Ti^{3+} ions (for e.g. Wright et al., 1963). Other workers suggested that rose color is due to intervalence charge transfer (IVCT) involving Ti-Fe ion pairs existing as structural impurities into the lattice (Smith et al., 1978). Later, Ma et al. (2002) attributed the rose color to IVCT between Fe^{2+} and Ti^{4+} occurring in specific sites of durmotierite ($Al_{6.5-7}(BO_3)(SiO_4)_3(O,OH)_3$) nanofibers present as inclusions in massive quartz. More recently, Kibar et al. (2007) suggested that rose color could be associated with impurity centers located in host lattice as well as in inclusions of durmotierite and chlorapatite ($Ca_5(PO_4)_3Cl$). This paper reports our first attempt to describe the mechanism of color changing in a massive rose quartz induced by γ irradiation coupling optical absorption, infrared and electron paramagnetic resonance (EPR) spectroscopies.

GEOLOGICAL SETTING OF TABOA PEGMATITE

The rose quartz sample investigated in this study is from the Taboa Pegmatite that is located in the Borborema Pegmatite Province (BPP), Northeastern Brazil. The BPP is one of the most important Ta-Nb-Be producer region in Brazil, associated to the production of industrial minerals (feldspars, quartz, micas, spodumens) and gemstones (aquamarines, tourmalines, garnets, rose quartz, among others). The Borborema Pegmatite Province (BPP) extends over an area of approximately 11.250 km^2, in the named Seridó Fold belt which is composed of gneissic-migmatitic basement of Paleoproterozoic age and the Neoproterozoic supracrustal sequence (Van Schmus et al. 2003), named Seridó Group that is constituted from bottom to top by Jucurutu, Equador and Seridó formations. It is accepted that

the pegmatites mineralized in gemstone and Be-Li-Ta rare element are of granitic composition and their formation is related to pegmatitic granites (Da Silva et al. 1995). These pegmatites are considered late- to post-orogenic in relation to the Brasiliano event. The mineralized pegmatites occur mostly as intrusions in the garnet-cordierite or sillimanite-biotite schists of the Seridó Formation, as well as in the underlying quartzites, meta-arkoses and metaconglomerates of the Equador Formation (Da Silva et al. 1995).

The Taboa pegmatite is located about 16 km west from the town of Carnaúba dos Dantas, in the state of Rio Grande do Norte. As it is shown in Figure 1, it consists in one conspicuous topographic elevation along the N-S direction. It is a discordant granitic pegmatite that outcrops as a body about 265 m long and 30-50 m wide, and strikes about N-S and dip either to the E or SE at 48º to 59°, having as country rocks the schists of the Seridó Formation. Taboa is a differentiated pegmatite with a wall zone 10-20 m wide and essentially composed of muscovite, biotite, garnet, black tourmaline and feldspars. The wall zone grades to an intermediary zone mainly composed of alkali feldspar and albite. Usually, there are replacements pockets of muscovite+quartz and biotite+muscovite+quartz+garnet surrounded by albite and tantalates in the contact between the intermediary zone and the quartz core (Figure 1). In the pegmatite core, the quartz color patches from milky to intense pinkish. Blue beryl crystals up to 1 m long are found in the quartz core (Figure 1). The quartz core was intensively exploited that resulted in an area of cave in southeastern portion of the pegmatite. The extraction of about 200 tons of gemological rose quartz has been reported by local explorers as coming from this or cave. Because of its bright color and transparence, the rose quartz from Taboa pegmatite has been exploited mainly for gemological purposes.

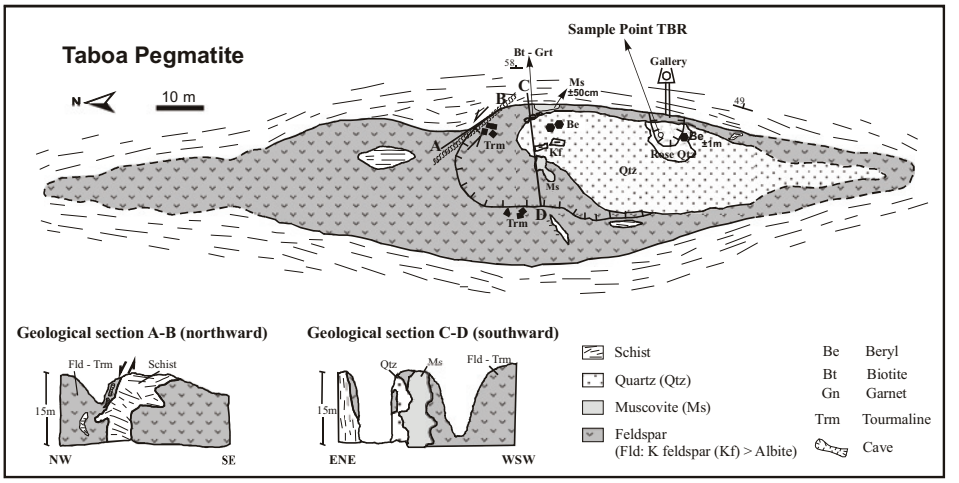

Figure 1 – Geologic sketch of the Taboa Pegmatite, BPP (Brazil) showing the location of the collected sample TBR used in this work.

EXPERIMENTAL PROCEDURE

Initially, a geologic sketch of the Taboa pegmatite was made in order to define the exact position of the sampling (Figure 1) in its internal structure. The collected block of massive rose quartz was sliced into small pieces with 12x12x3.5 mm using a diamond saw. The sample pieces (hereafter named samples) were lapped and optically polished with Al_2O_3 and its final thickness was close to 3.0 mm. Later, the samples were irradiated with γ-rays with doses ranging from 0.5 to 64 kGy. The irradiations were carried out at room temperature using an irradiator of ^{60}Co with 7.6 kGy.h^{-1} dose rate. The color change was accessed by optical absorption spectroscopy with an unpolarized beam using a Lambda-35 Perkin-Elmer™ spectrometer. Optical spectra were measured prior and after irradiation. In order to reduce the effect of the fracture pattern on the optical absorption, a window of 3 mm was positioned between the sample and detector. The absorption bands were evaluated by the Beer-Lambert formula.

OH-related defects in Taboa quartz were analyzed by infrared (IR) spectroscopy, carried out at room temperature with an unpolarized beam using a FTLA2000ABB Bomen™ spectrometer. Each spectrum was recorded after 50 scans from 6000 to 500 cm^{-1} with a resolution better than 4 cm^{-1}. For EPR spectroscopy, the samples were sectioned into two parts and 60 mg of powder in the size fraction 75-150 μm was prepared. The measurements were carried out at room temperature with a Bruker EMX-Plus spectrometer operating in the X-band. After sweeping a broad filed range, EPR signal was collected from 3440 to 3560 G. For some samples, the EPR signal was recorded as a function of the microwave power ranging from 0.5 and 20 mW. The intensities of parallel and perpendicular EPR lines of the powder spectra were estimated for a non saturated condition.

RESULTS AND DISCUSSION

Figure 2 shows optical, IR and EPR spectra of rose quartz from Taboa pegmatite. In the as-received condition, only the absorption band near 197 nm is observed in the optical spectra. As it was previously reported above, this band is associated with the IVCT between Fe and Ti ions. By increasing the irradiation dose, this band decrease and absorption bands near 230, 460 and 620 nm became observed in the optical spectra. These bands are better noticed in the inset plot of Figure 2(a) which shows the net effect of γ irradiation in the optical absorption. According to previous investigations with natural rock crystals and synthetic quartz, the band at 230 nm is related to E' type center whereas 460 and 620 nm bands are related to the EPR signal of $[AlO_4]^0$ center (Weil 1984; Halliburton 1985).

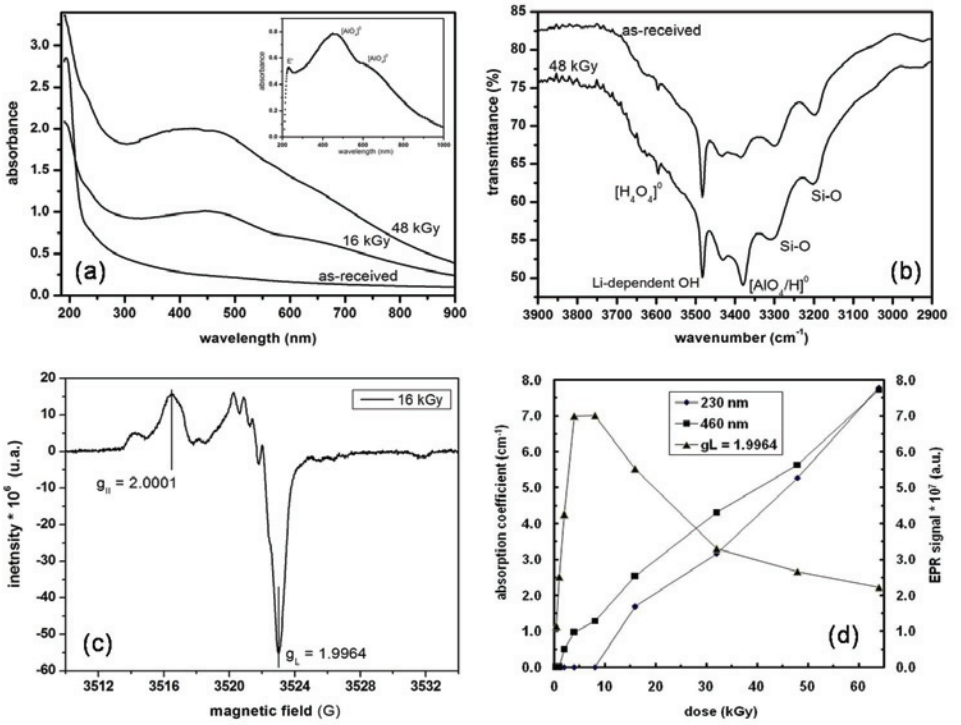

Figure 2 – Optical (a), IR (b), EPR (c) spectra of rose quartz and the relationship between optical absorption and EPR signal with high γ doses (d).

Figure 2(b) shows typical IR spectra obtained prior and after irradiation. The absorption bands attributed to Li-dependent OH (3484 cm^{-1}) and $[H_4O_4]^0$ centers (3585 cm^{-1}) are observed in both conditions. Different from rock crystals issued from hydrothermal veins, the absorption at 3484 cm^{-1} was not reduced with high γ doses (Guzzo et al. 2009). On the other hand, the IR band attributed to $[AlO_4/H]^0$ appearing at 3380 cm^{-1} became better observed after irradiation with doses higher than 2 kGy. This dose level corresponds to the onset of the optical bands related to $[AlO_4]^0$. As it was previously shown, $[AlO_4]^0$ and $[AlO_4/H]^0$ centers are formed by the dissociation of Al centers compensated by alkali ions (mainly Li^+) labeled as $[AlO_4/M]^0$ centers (Halliburton 1985; Guzzo et al. 2009).

The EPR spectrum of irradiated rose quartz in Figure 2(c) reveals several lines from 3512 to 3532 G. Two of these lines were assigned to parallel and perpendicular powder signals of the $[GeO_4/Li]^0$ center previously identified in irradiated rose quartz (Weil 1984). It was observed that this signal increases with the increasing of γ dose up 8 kGy and then decreases. In the as-received condition, any EPR signal that could be associated with Fe or Ti centers was observed. The origin of the other lines appearing in Figure 2(d) could not be identified.

Figure 2(d) summarizes the effect of the γ irradiation on the intensity of the point

defects identified in optical and EPR spectra. It is observed that the onset of $[AlO_4]^0$ center occurs at lower doses than the E' type center. No evidence of saturation was observed for these bands even after 64 kGy. The increasing in the optical bands related to $[AlO_4]^0$ explains the smoky color increasing observed in irradiated samples. The EPR signal associated to $[GeO_4/Li]^0$ appears after irradiation with 0.5 kGy, reaches a maximum at 8 kGy and then decreases. The origin of this center can also be associated with the dissociation of $[AlO_4/Li]^0$ which acts as precursor for $[AlO_4]^0$, $[AlO_4/H]^0$ and $[GeO_4/Li]^0$. Unfortunately the EPR signal of $[AlO_4]^0$ is accessed only at low temperatures. Due to some mechanism that cannot be elucidated now, the formation of E' centers can be associated with the decrease of $[GeO_4/Li]^0$ centers.

SUMMARY

The irradiation with γ rays did not change the rose color saturation of Taboa pegmatite and gave rise to smoky color. Similar as found in rock crystals, the color changing was associated with the formation of $[AlO_4]^0$ and $[GeO_4/Li]^0$ centers. The decrease in the absorption band connected with the IVCT between Fe and Ti ions was observed up to irradiation with 16 kGy.

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