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GAMMA IRRADIATION OF QUARTZ FROM PARANA BASIN, SOUTH AMERICA

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ABSTRACT

The use of gamma radiation to induce or enhance color centers in gemstones is a widespread technique and applied worldwide on a industrial scale since at least 1970. The presence of defects and defect structures in quartz from a border region of southern Brazil and Uruguay are the reason for the creation of a new color variety of quartz called "Prasiolite" in the gem trade. This quartz has a pleasant green color produced by gamma irradiation. The procedures of irradiation at IPEN show that the activation of these color producing defects can be monitored by detailed chemical and spectroscopic analysis. For the first time UV-VIS-NIR spectra of this new color variety of quartz are shown. They revealed special features of these quartz crystals coming from basaltic terraines of the Parana Basin. Contrary to most specimen of quartz from other parts of Brazil, they have such a high water and OH content that they resemble more chalcedony or opal, but not highly crystalline quartz specimens. The cause of the color are broken bonds of Si-OH defining the so-called dangling bonds.

1. INTRODUCTION

The implantation of a compact multipurpose industrial type gamma irradiator of small size and continuous operation possibilities at the Radiation Technology Center of the Instituto de Pesquisas Energeticas e Nucleares (IPEN-CNEN/SP) in São Paulo, Brazil [1] opened the way for systematic studies of the application of gamma- irradiation in industrial processes. Standard methods of sterilization of medical materials, polymers and rubbers as well as polymerization processes of resins are already being applied on a semi-industrial scale or their procedures are studied to optimize the run conditions. Since the semi-industrial irradiation phases of the plant are mainly during daytime and restricted to normal weekly rhythm, there is much time left to explore the use of the gamma irradiation in material science by exploring the effect of ionizing radiation on chemical substances, metals, ceramics and , not the least, on minerals and gem material since Brazil is famous for its richness in precious stones.

These latter studies are in line with actual national efforts to increase the value of abundant rough gem material without special features by different types of treatments. Ionizing radiation is known to induce or enhance color centers in gemstones, a fact already known for a long time [2]. To cite an example, most of the blue topaz sold today as a gemstone is produced by gamma or neutron irradiation. Also, quartz, a very common mineral in Brazil, is being treated at irradiation centers on a commercial basis in Brazil and abroad to produce what is known today as gem varieties called " Greengold " or " Cognac", two types of greenish yellow and brown color produced by gamma irradiation and subsequent heat treatment [3].

This paper presents preliminary results of the production by gamma irradiation of a newer type of color variety of quartz, called "Prasiolite" in the trade, and its characterization . The leek green color of this quartz is the reason for its name.

2. MATERIALS AND METHODS

Some information will be given about the material used , the irradiation procedures and the methods of characterization.

2.1. Materials

Quartz, or more precisely α-quartz, the modification of SiO2 stable at normal conditions until about 573° C, is a tectosilicate with three dimensional arrangement of polymerized tetrahedrons of SiO_4. It can form right handed or left handed crystal forms due to the steric sense of its crystal class. Under most growth conditions, twin intergrowth between these two forms will occur giving rise to growth defects. Quartz is one of the few minerals with a high degree of chemical purity, the amount of elements which can be included in the structure or can substitute the silicon ion is generally much below one percent by weight. But even these small amounts are enough to create colored varieties like amethyst and citrine in nature.

Quartz is one of the most abundant minerals and its formation conditions are quite varied. It appears as overgrowth in the sedimentary cycle, as crystals in hydrothermal and metamorphic systems and in granitic- pegmatitic associations with tourmaline, micas and beryls. Since each growth regime will have its own chemical imprint, it will be obvious that the type of trace elements included in the crystal will be unique. Quartz derived from granitic rocks and formed at relative high temperature will have included mainly Li, Na, K, Al , Ge but very little water or hydroxyl. On the other hand quartz derived from hydrothermal regimes will show a chemistry dominated mainly by Fe, Al, water and hydroxyl. The defect chemistry, which will determine the final color by any treatment, will therefore reflect these growth conditions. The quartz used in the present work 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 near the towns of Artiga and Quaraí at the border of Brazil and Uruguay. The quartz material, generally of euhedral shape or fragments of crystals, was collected and send by gem dealers for irradiation treatment tests.

2.2. Irradiation procedures

The batches of quartz were submitted to irradiation in the Multipurpose Irradiator of ^{60}Co of the Radiation Technology Center (CTR) from IPEN-CNEN/SP. 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 13 sources of ^{60}Co as shown in Fig. 1.

Figure 1. Irradiation space at the Multipurpose gamma-Irradiator at IPEN-CNEN/SP

The total dose of gamma radiation applied to these batches is variable. Maximum doses applied were up to 650 kGy. 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 "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 samples marked PB are from southern Brasil, MG and GE are a natural quartz from Minas Gerais and a fused , very pure Silica from the firm General Electric. These latter materials served as reference material. The chemical composition has been analyzed by standard methods of ICP-Mass-Spectroscopy (Elan-6100DRC, Perkin Elmer) at the Chemical Laboratory of the Geoscience Institute of USP, by ICP-AES at IPEN and NAA at NNA-Laboratory of IPEN. 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 some measurements of photoluminescence (PL) at the Laboratory of the Chemical Department, USP after standard treatment of the samples.

3. RESULTS AND DISCUSSION

3.1. Chemical composition

All quartz samples had Fe (32 to 949 ppm), Al (612 to 1648 ppm), Na(350 to 1070 ppm), Mg (105 to 286 ppm), Ti (33 to 174 ppm) and Li (7,9 to 28 ppm). They represent three irradiated samples from Parana Basin (PB1 to 3) and one sample of a quartz from Minas Gerais, taken from a quartz vein intercalated in granitic rocks near Curvelo. Generally, the overall trace element content is lower in the PB samples, but all samples have iron and alumina , the two most important chemical elements to produce color centers in quartz. The overall pattern of trace elements is characteristic of the origin of these crystals, hydrothermal formation. The GE 124 sample has 14 ppm Al, 0,2 ppm Fe, 0,7ppm Na and 1,1ppm Ti and 0,6 Li . It can be considered very pure.

3.2. VIS-NIR Spectroscopy

The Fig. 2 shows the combined spectroscopic results of a green, irradiated quartz (PB), the vein quartz from Minas Gerais (MG), and for comparison purposes, the spectrum of the industrial ultrapure fused Silica, GE 124 in the wavelength range of 1200 to 3000 nm. Comparing the three spectra , one notes some similarity between the GE and the PB sample. The MG sample, however , is different. The latter shows Al and Li related features near 3000 nm [4] which are absent in the spectra of the other samples and a lack of features in the range of 1200 to 2500nm.

One notes the very high M-OH peak at about 2300 nm. In this , as well as in the 1400 nm region are mainly the first overtones of the Silanol groups (Si-OH) [5]. It appears from this that the quartz from southern Brazil is quite different and much more hydrous than the pegmatitic quartz from Minas Gerais. Indicated in Fig. 2 is also the peak of molecular water at about 1900 nm [6].

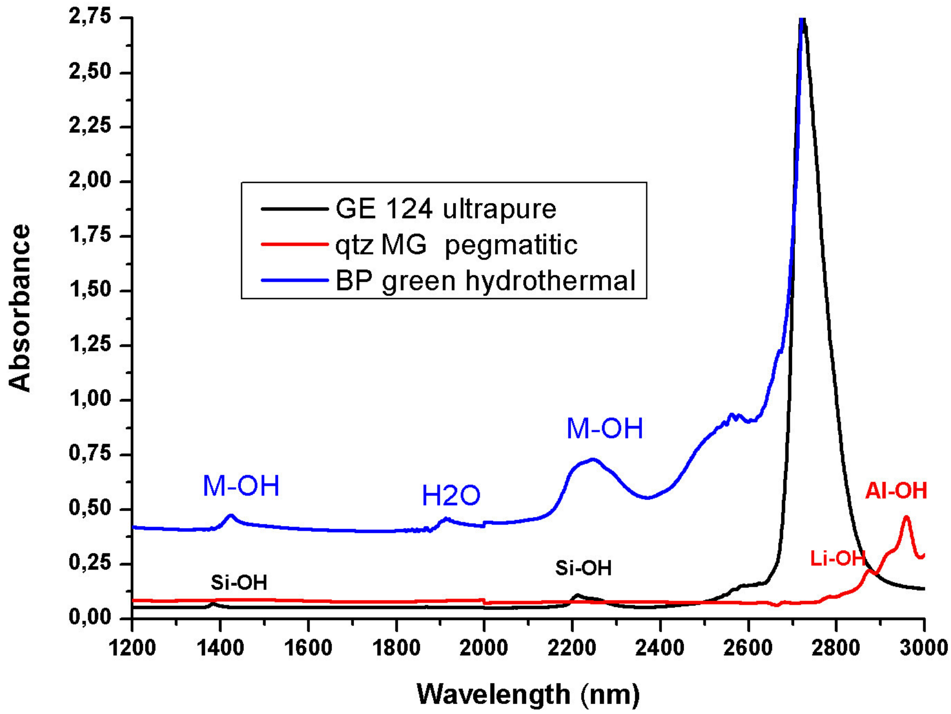

Figure 2. Near InfraRed spectra of different quartz types.

This high water and OH content of the quartz from southern Brazil is unique and only synthetic quartz [7] , sol-gel derived silica samples [6] or microcrystalline quartz show similar features. It appears from the spectroscopic evidences that the high water content overrides the influences of Fe and Al contained in the samples.

Fig. 3 shows the UV-VIS-NIR spectrum of an irradiated green quartz.In this case spectra have been taken parallel and at right angle to the optic axis to explore the possibilities of pleochroism of the OH absorption. In the visible range the spectrum shows an absorption peak at 592 nm with an linear absorption coefficient of 0,2 cm-1. It is this absorption which produces the green color. The position is very different from all peaks known for amethyst or citrine [3,8] and varies slightly from 614 to 592 nm for different samples. Besides, the absorption coefficient is dose dependent. Less radiation produces less absorption and , consequently, a less saturated green. Since neither iron nor alumina absorbs in this range, but only non-bridging oxygen bonds(NBOHC), a photoluminescence run has been used to prove the 650 nm light emission, characteristic of these NBOHC.

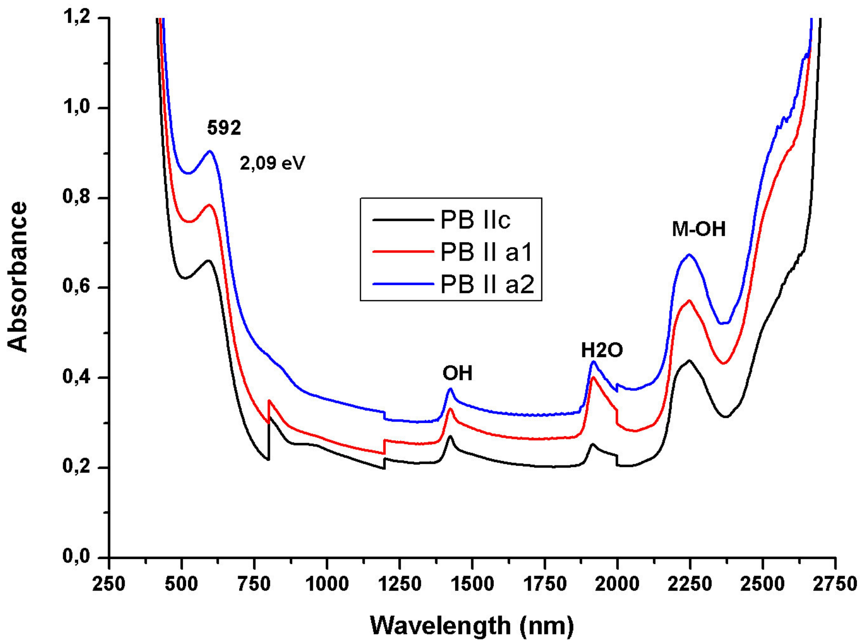

Figure 3. UV-VIS-NIR spectrum of a green, irradiated quartz from southern Brazil.

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