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CHARACTERIZATION OF COLOR CENTERS IN QUARTZ INDUCED BY GAMMA IRRADIATION

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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 much colored commercial varieties. Quartz occurs in Brazil mainly in two geological environments, called pegmatitic and hydrothermal. The detailed mechanism of color center formation of these two types of quartz will be investigated by spectroscopic and chemical analysis. Until yet, it can be shown that due to chemical differences of the nature of mineral forming fluids, the two types behave differently. All quartzes contain mainly traces of Iron, Aluminum, Lithium and some amounts of Water. The quartz of hydrothermal origin incorporated much structurally bound water , and despite some similarities with the chemical composition of pegmatitic quartz, this high water content is the reason for the formation of Silanol radicals, giving the green color to the quartz. The main difference in chemical composition of pegmatitic quartz is the presence of higher amounts of Al and Li , responsible for the brownish and yellowish colors formed by irradiation. Since each pegmatite is different, the quartz will behave differently. This explains the formation of the famous “Green Gold” of quartz from São José da Safira , and the more yellowish, Citrine type, color of quartz from the Coluna deposit, near Itamarandiba, Minas Gerais.

1. INTRODUCTION

Color enhancements by use of radiation and subsequent heat treatment is today a very widespread method to increase the amount of gem material by using commercially less valuable qualities. As radiation, one may use electron, neutron or gamma rays. The former two types are more effective by inducing higher quantities of defects, but their drawback is the formation of radioactive daughter elements in gemstones. This needs quite long storing times until the level of induced radiation has decreased to such low levels permitted by the official agencies. One of such case is Topaz, which acquires his blue color by such treatments but needs storage times up to 2 years.

This is not the case by use of gamma radiation. No radioactive elements are produced, but the intensity of gamma ray is much less and more time is needed to produce similar effects. During the last decades, however, the use of quite strong Co-60 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 “Greengold” or Lima quartz, the “Champagne” or “ Beer” colored, the green colored variety called “ Prasiolithe” and the blue to blueviolet quartz called “Safirite or Blueberry Quartz”. These new colors have increased the use of quartz for jewelery purposes and aroused new interest in the properties of this mineral.

The structure of quartz is quite simple. Units of SiO4-tetrahedras are stacked along the c-axis either by right handiness or left handiness, forming connected chains of hexagonal or trigonal symmetry with channels parallel to the c-axis or inclined to it by 60 degree. The small ionic size of silicon does not permit his substitution by much elements except mainly trivalent iron, aluminum, phosphorous and germanium. Quartz is therefore a quite pure mineral and , as shown by Iwasaki et al [1] and Guzzo [2] , may contain inclusions and impurities classified as mineral or fluid inclusions and as structural units. Those structural impurities, mainly responsible for the color centers, may be substitutional or interstitial. As shown by the authors above, they are Fe^{3+}, Al^{3+}, OH^- and H_2O molecules as substitutional and Na^+, Li^+ and H_3O^+ as interstitial units located in the channels of the structure. The substitution of tetravalent Si by trivalent ions necessitates the presence of univalent cations to maintain charge balance. Figure 1 illustrates this scheme [3].

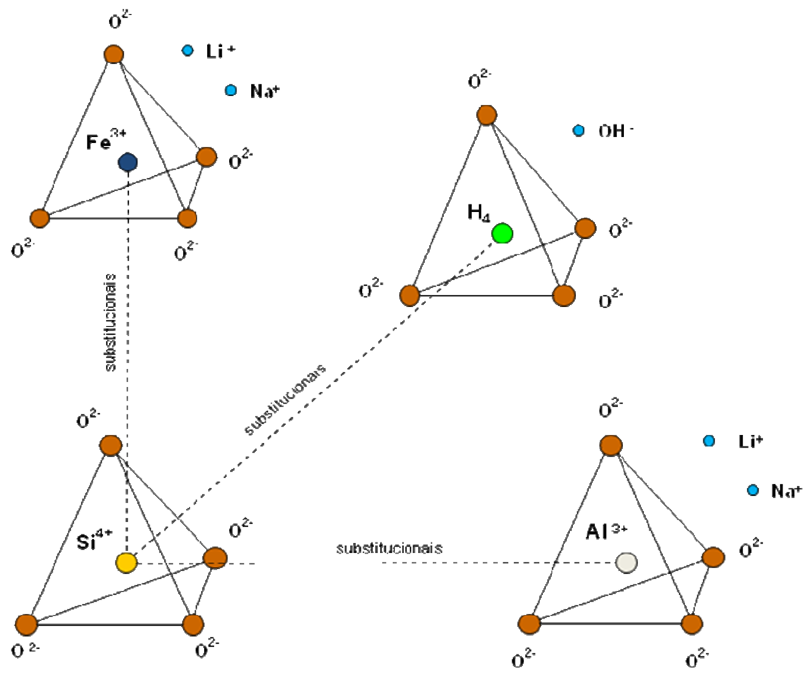

Figure 1. Scheme of substitution and charge balance in quartz.

Quartz of gemological quality found in Brasil and used for these treatments is mainly found in two geological occurrences, the hydrothermal deposits of the basaltic rocks of the Paraná Basin and of the quartzitic Serra de Espinhaço Range and the deposits of the long Pegmatitic Belt as shown by Chaves et al. [4] , and tied strongly to granitic rocks and of igneous origin.

The Hydrothermal Deposits contain all the varieties of silica found in fractures and geodes of the basaltic and felsic volcanic rocks of the huge Parana Basin, stretching from Argentine to Rio Grande do Sul, Parana, Santa Catarina, São Paulo, Mato Grosso and eastern Minas Gerais 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, stretching from southeastern Minas Gerais to northern Bahia. Famous are the quartz crystals and the smoky quartz from Minas Gerais as well as the amethyst from Montezuma, northern Minas Gerais, which turns green by heating and blue by irradiation.

The pegmatitic deposits are found near large granitic batholiths scattered along a large belt covering the states of São Paulo, Rio de Janeiro, western Minas Gerais, Espirito Santo and Bahia. Silica varieties found in these igneous deposits are mainly rose quartz, smoky quartz, citrine and the few incolor quartz types which produces the much sought after greenish yellow gemstones called “Green Gold” or “Lima quartz”. Of these only two are known today, located at São José de Safira and Itamarandiba, Minas Gerais.

2. MATERIALS AND METHODS

The samples used are from hydrothermal and pegmatitic occurrences and are mainly provided by the commercial companies Murta Gems (Minas Gerais) and Stoll (Rio Grande do Sul), interested in the treatment.

The irradiation has been made in the Multipurpose Irradiator of the Radiation Technology Center from IPEN-CNEN in São Paulo [5] . The equipment has actually 32 sources of Co-60 producing a total of irradiation of 220 000 Ci. The samples have been irradiated to about 900 kGy, after which most had been saturated .

3. CHARACTERIZATION OF THE MATERIAL

Some of the material has been analyzed to have control on the chemical composition and their influence on the colors produced by irradiation and heating . Standard techniques of Inductively Coupled Plasma Atomic Emission Spectrometry - ICP-AES and Neutron Activation Analysis - NAA have been applied, with the former at Environmental and Chemical Center - CQMA and the latter at Neutron Activation Analysis Laboratory - LAN of the IPEN-SP. Visible and Near Infrared Spectroscopy – Vis-NIR has been done at the Ionic Crystal Laboratory of the Physics Institute at USP-SP.

4. PRELIMINARY RESULTS AND DISCUSSION

The preliminary chemical results have confirmed that the crystal chemistry of the hydrothermal quartz is mainly dominated by substitutional impurities of iron, alumina and hydroxyl or molecular water, in line with data shown by Guzzo [2] . This quartz will show a green color by irradiation or, sometimes and by doses higher than 400 to 600 kGy, a grayish tinge as shown in Figure 2.

Figure 2. Hydrothermal quartz , natural crystal without color, green colored crystal produced by irradiation to 450 kGy and a smoky green color produced by the same dose.

No explanation for the grayish hue of some samples has been found yet. The relative high amount of alumina shown by chemical analysis of some material may be responsible. As shown by Schultz-Guttler et al. [6] the green color is produced by NBOH, or non bonding oxygen bonds. The details of this color center needs still further study.

Observations of large numbers of samples have shown that some does not acquire any color, others may have been partially colored, with the tips of the crystal a deep green and the bottom colorless, or sometimes, nearly all crystals had a grayish cast. There does not exist any systematic study correlating the chemistry of those crystals with the intensity of color produced. It may very well be that there exists more than one type of color center. The few chemical analyses of pegmatitic quartz samples showed high alumina contents, in line with data given by Iwasaki [1] and Guzzo [2] .

Colors obtained by irradiation and subsequent heating of some material from Itamarandiba (Minas Gerais) are quite intense as shown in Figure 3.

Figure 3. Quartz crystals from pegmatite, Itamarandiba, above from left to right, colorless, blackened by irradiation to 1000 kGy, and heated at 260 degree for 1, 2 and 3 hours. Shown also cut gemstone.

These colors are quite similar to those of material from São José de Safira, studied by Nunes [7] . He showed that the yellow color is produced by Al for Si substitution and charge balance by Li. Again, no systematic study has been undertaken to correlate chemical composition to shade and depth of color. Figure 4 shows the greenish hue of the so called “Green Gold” gem variety of quartz, a color studied by Nunes [7] . The VIS-NIR spectra of this material, Figure 5, shows a typical absorption by iron. It may well be that this color is produced by an interplay of Al and Fe substitutions in quartz. Figure 1 above shows some of the possibilities.

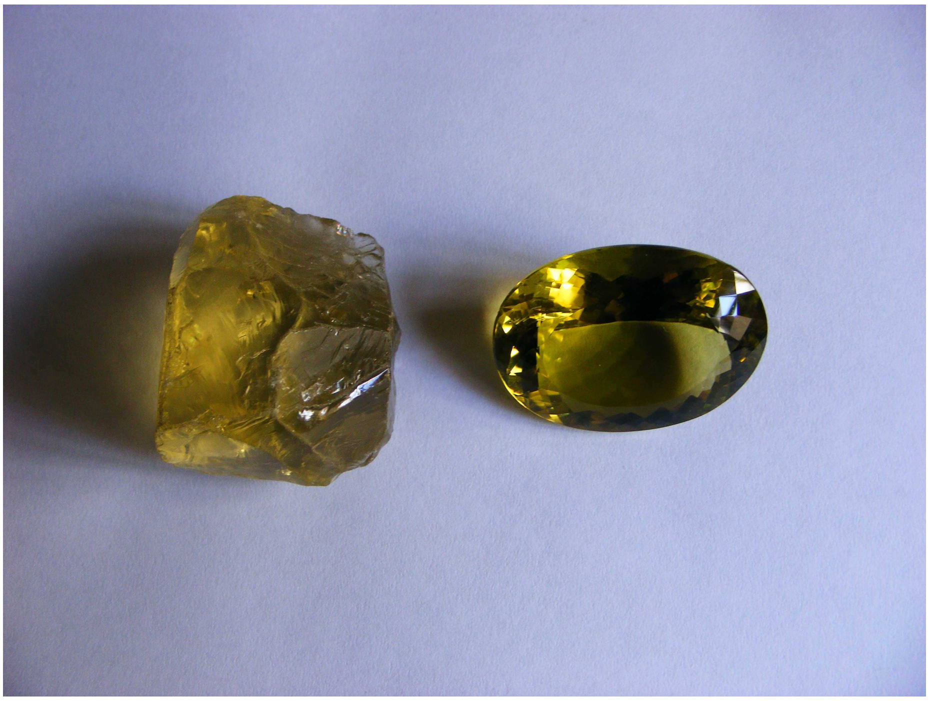

Figure 4. Greenish yellow variety of pegmatitic quartz, called “Green Gold”, irradiated and heated in the rough and cut.

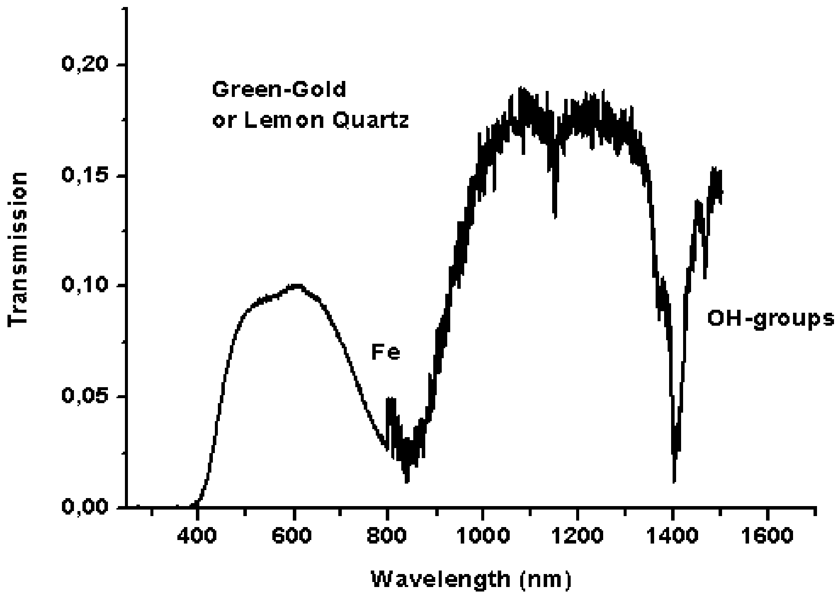

Figure 5. VIS-NIR spectra of “ green gold quartz”

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