

IDENTIFICATION OF COLOR DEVELOPMENT POTENTIAL OF QUARTZ BY RAMAN SPECTROSCOPY

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ABSTRACT

Colorless quartz is usually exposed to ionizing radiation (gamma rays or high energy electron beams) to acquire different colors for jewelry. Color development is due to the presence of traces of some elements such as aluminum, iron, hydrogen, lithium, or sodium. Most quartz crystals are extracted colorless from nature and it is necessary to separate those that can develop colors from those that cannot. Irradiation tests can be used to accomplish this separation, but they take a long time. Infrared signature of colorless quartz can also be used. However, infrared spectroscopy is quite expensive, especially when using portable devices. Raman spectroscopy is now available as an inexpensive and portable technique that could provide identification of the samples of colorless quartz still in the field, facilitating the prediction for their economic exploitation. In addition, Raman spectroscopy usually requires a minimum or no sample preparation. This paper presents an investigation of the feasibility of using Raman spectroscopy as a substitute for infrared spectroscopy to predict the potential for color development of quartz. A band at 3595 cm^{-1} in the Raman shift spectrum was observed only along the c axis of a prasiolite excited by a high power 514 nm laser. This band was not observed in quartz samples that do not develop color after irradiation. Further studies are required to identify the potential for color development by Raman spectroscopy of other types of colorless quartz.

1. INTRODUCTION

Amethyst, prasiolite, citrine, and morion are gemstones widely used in jewelry, to compose mineral collections of museums or private owners, or used to decorate homes and offices. They are all alpha quartz [1] and the differences between them are very small. Natural quartz always has trace elements in its crystal lattice, such as aluminum, iron, hydrogen, lithium, sodium, and potassium. The content of these trace elements is important for the development of color. However this requires exposure to ionizing radiation, otherwise these trace elements are not able to produce colors in quartz.

Since the discovery of radioactivity, it has become clear that the color of several minerals, including quartz, can be modified by their exposure to the radiation emitted by radioactive substances [2-3]. Jewelry demands tons of colored quartz that cannot be found in nature. It is necessary to extract colorless quartz from nature and to submit it to irradiation and heating. The problem is separating the quartz that can develop colors of commercial value from the quartz that cannot.

Usually this separation is done through irradiation tests of representative samples. These tests can take weeks, because the samples need to be sent to an irradiation facility to be irradiated to different doses. After irradiation, the irradiated samples need to be sent back to the owner, who must apply a heating process (in some cases) and evaluate the color quality. Another issue is that some irradiators do not specify the applied doses [4].

The transmitted infrared spectroscopy by Fourier transform (FTIR) signature of colorless quartz can be very valuable in indicating whether or not it can develop colors. Through a previous correlation with results of irradiation tests [5], it is possible to predict the color that will be achieved after an irradiation dose. These analyses take only few minutes and can be performed close to the mining site if a FTIR spectrometer is available.

Infrared measurements were widely reported in electrodiffusion studies of quartz containing alkalis [6]. The purpose of these studies was to understand the electronic performance of cultured quartz for the electronic industry. There are few studies concerning color formation. Nunes et al. [5] and Lameiras [4] reported detailed information about the interpretation of FTIR spectra of colorless quartz with the aim to estimate their potential for the development of color after irradiation. In addition they also proposed a mechanism for the formation of color in quartz. The region of interest is from 2400 cm^{-1} to 3650 cm^{-1} .

The analysis of the absorption spectrum in the infrared region of natural colorless quartz crystals allows evaluating its chemical composition and predicting the color of the crystal after irradiation and heat treatment. This analysis is routinely employed in CDTN/CNEN using FTIR to identify the potential of colorless quartz samples to develop color [4-8].

Raman spectroscopy is a great candidate for these types of analyses due to its lower cost and portability. It is a technique that uses inelastic scattering of light to study the vibrational properties of molecules or crystals [9]. In some applications, Raman spectroscopy offers advantages over FTIR. In general, it requires a minimum or no sample preparation, the sample can be transparent or not, and size may range from $1\text{ }\mu\text{m}^3$ to some dm^3 . Furthermore, surfaces with different textures can also be analyzed [10]. On the other hand, advances in technology are enabling designs of a new generation of portable Raman systems ideal for field work. Over the last 20 years Raman spectroscopy has been established as an important technique for mineralogy and geochemistry due to its simplicity, rapid measurements, and low cost.

The aim of this work is to verify the use of Raman spectroscopy to evaluate the potential of color development of colorless quartz. The quartz dealers have the desire to perform the identification of color development potential in field, during the extraction of quartz, using portable equipments. Due to the lower cost of portable Raman spectrometers, the use of this technique is being considered as it is regularly used by geologists to identify different minerals.

Currently, the main disadvantage is that Raman spectroscopy is less sensitive than FTIR to the presence of impurities in quartz. Raman spectroscopy has been effective identifying minerals, e.g., distinguishing quartz from other minerals. However it has not been exploited as a tool to differentiate colorless quartz with different potentials to develop color. This is due to the fact that Raman spectroscopy is not still sensitive enough to chromophore impurities when they are present in quartz in amounts of ppm - parts per million.

2. MATERIALS AND METHODS

2.1 Pre-selection of samples due to color development potential

Eleven different samples of natural colorless quartz with known potential for color development were selected. They were denoted from A to K. Two standards of colorless quartz before and after irradiation with very low impurity levels were chosen as reference, and were labeled as P01 and P02. The two samples are from the region of Diamantina-MG. Before analysis, these quartz samples were irradiated to observe the developed color. After irradiation they were heated to become colorless again and then the infrared spectrum was measured to classify the samples according to their potential of color development, as already mentioned [5]. The normalized FTIR spectra obtained at room temperature are shown in Figures 1-5. Measurements were done directly in a sample fragment, without dilution in KBr. The spectra were classified according the color achieved after irradiation and heating.

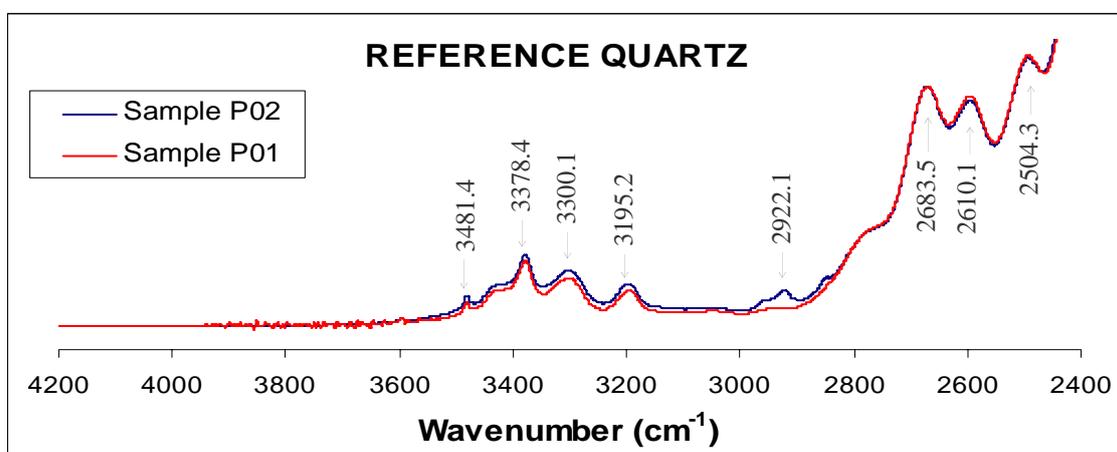


Figure 1: FTIR analysis of the reference natural samples that will remain colorless after irradiation.

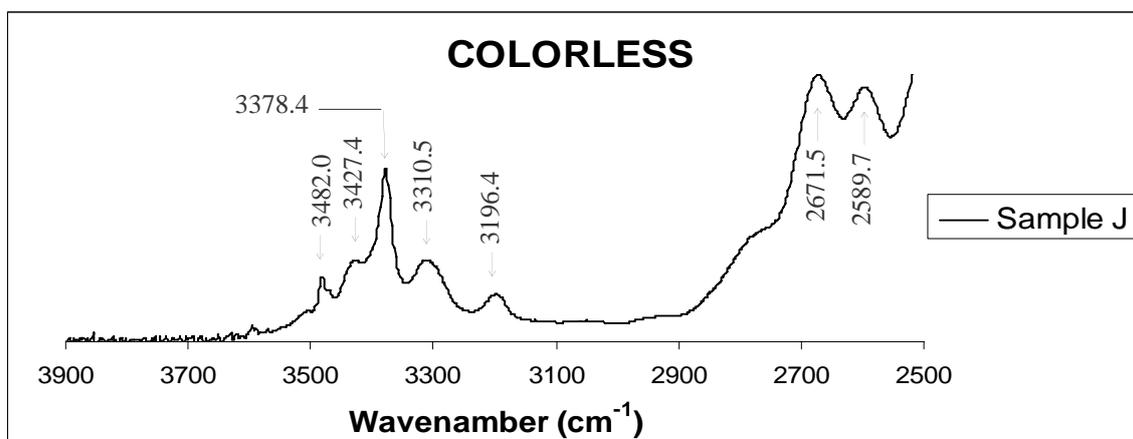


Figure 2: FTIR analysis of colorless sample J that will either acquire a slightly grayish or black color after irradiation and colorless after heating.

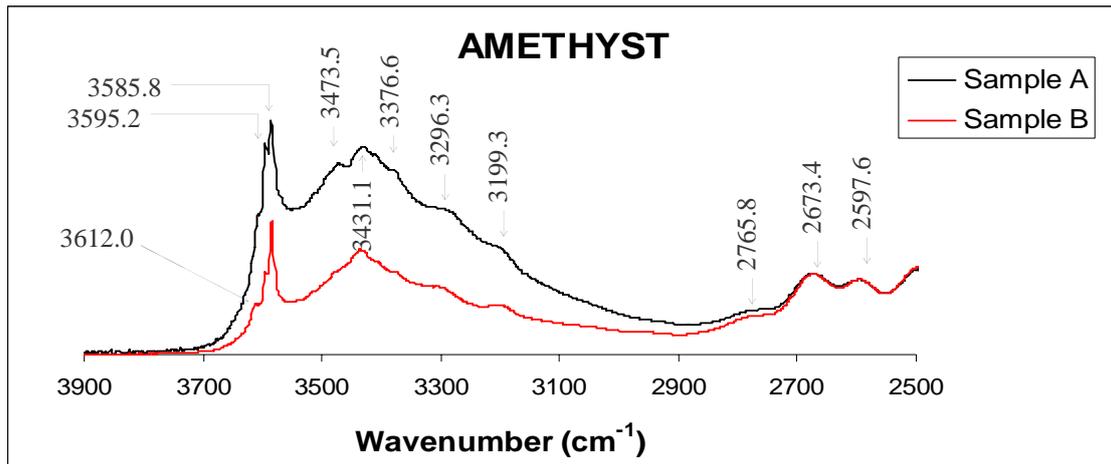


Figure 3: FTIR analysis of the colorless samples A and B that will develop violet color after irradiation.

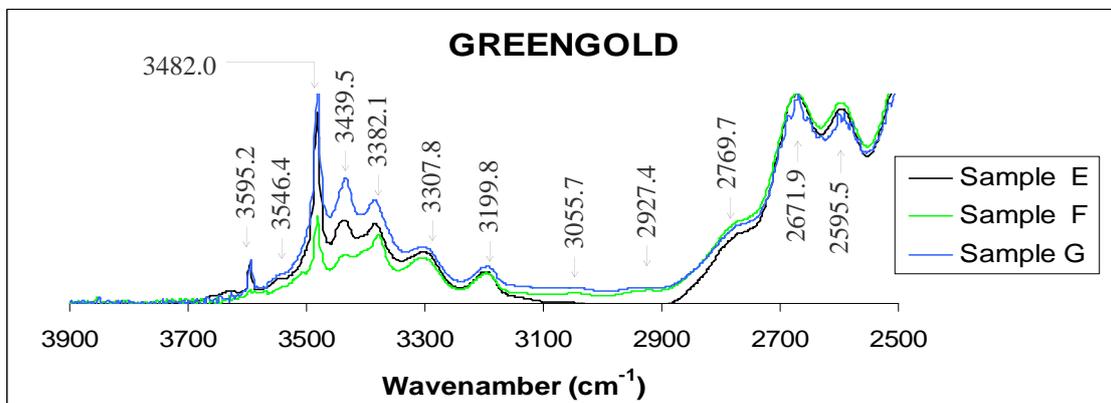


Figure 4: FTIR analysis of the colorless samples E, F and G, that will develop black color after irradiation and green gold, or brown after heating.

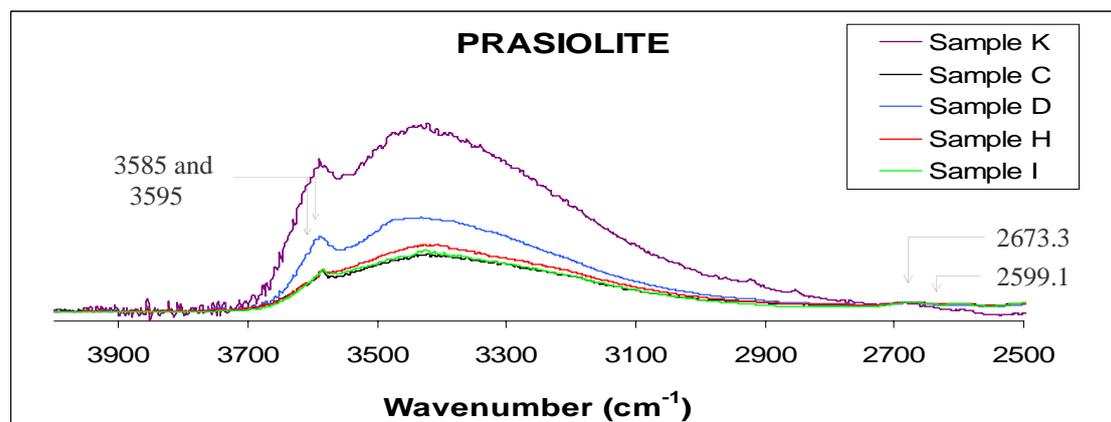


Figure 5: FTIR analysis of the colorless samples C, D, H, I and K that will develop green color after irradiation.

After this classification, the Raman shifts of these samples could be grouped according to the similarities in their spectra. All Raman analyses were performed simulating the actual conditions found in field with a Portable Spectrometer, such as, unoriented samples, low acquisition time and low power depolarized laser. Under these analysis conditions, it was not possible to appreciate differences among the colorless quartz spectra. It was noticed that the Raman spectroscopy could distinguish only the alpha quartz lattice. Any other vibrational signals of interest for the determination of their potential to develop color, if any, were masked by measurement noise, due to the dilution of those impurities related to color change by irradiation. The color development potential in colorless quartz could not be identified. These results were already published [11]. The differences among the spectra in that paper were due to the sample orientation under the laser beam. These differences were already expected [12-13] because of the anisotropic behavior of quartz. These measurements were repeated and analyzed with special conditions in an attempt to identify color-causing impurities.

2.1. Raman analysis with special conditions

More in-depth investigations of possible hidden bands within measurement noise were made in order to check if Raman spectroscopy would be able to resolve some of those bands, such as, vibrational modes of the charge compensators like Li, H, Na, K, and $[\text{AlSiO}_4]^-$ and $[\text{FeSiO}_4]^-$ centers. The acquisition conditions were set in order to improve the signal-to-noise (SNR) ratio.

Tests were done using high power depolarized laser of 514 nm to excite the samples. Also, measurements were made with a long acquisition time and a greater number of accumulations. The grating of the apparatus was fitted with a smaller number of lines to improve the intensity of the signal received by the CCD, and the signals were collected by the single window mode in the region most likely to detect impurities: $(3000 - 4000) \text{ cm}^{-1}$ [4-5]. This range restriction was necessary to prevent high bands below 1500 cm^{-1} exceeding the detection limit.

The colorless sample K, a prasiolite in potential, was selected since it has the strongest FTIR impurities (Figure 5). The P01 and P02 standards were taken as reference due to their lower impurity signals (Figure 1).

Figure 6 compares the Raman shifts and FTIR spectra of prasiolite K. Raman measurements were performed in a Horiba Jobin Yvon Micro Raman. These Raman spectra were obtained using a 514 nm laser at 10 mW, a 10x objective and 180 lines/mm grating. The FTIR of sample K is the same as in Figure 5, showing the region of wave numbers greater than 1500 cm^{-1} region. The spectra were arranged in this order to facilitate visualization. The intensity is relative and the baseline has not been fitted (this also applies to Figure 7 and Figure 8).

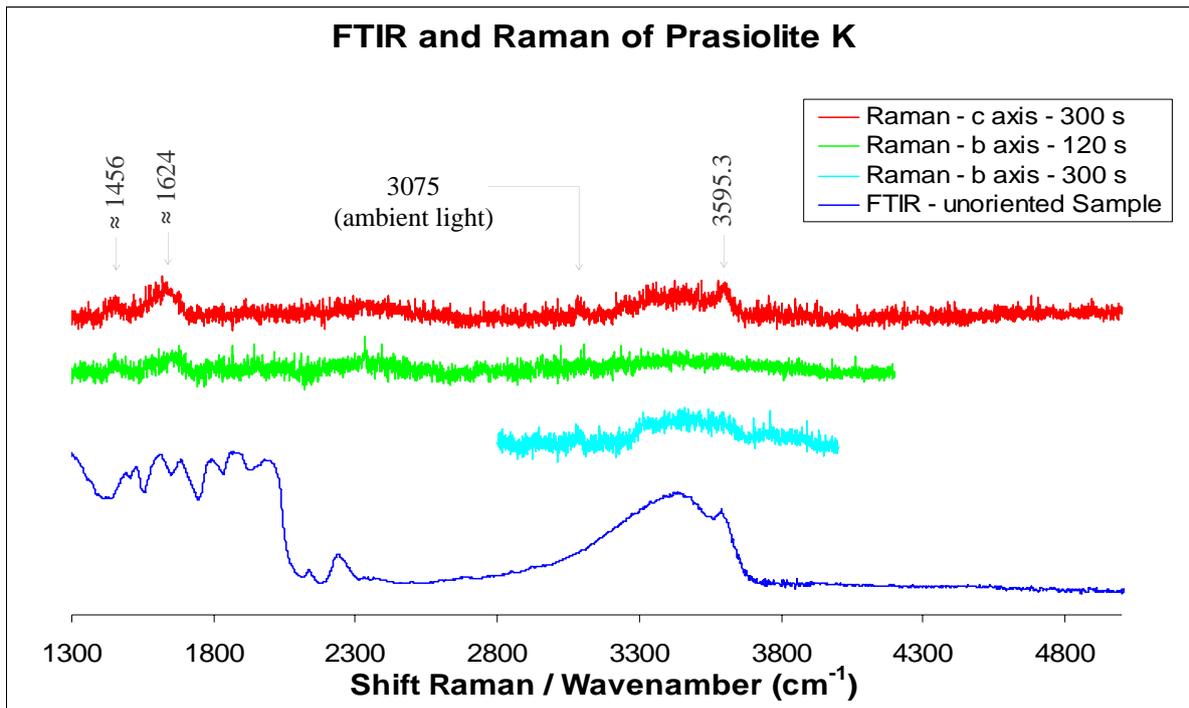


Figure 6: Comparison between Infrared and Raman spectra of sample K. The time of acquisition and sample orientation varies according to legend.

The following measurements were performed to confirm the presence of the 3595 cm⁻¹ band and its occurrence in quartz that remained colorless after irradiation. Figures 7 and 8 compare the Raman spectra of sample K with P01 and P02, measured in spectrometers with higher efficiencies and larger SNR. The spectra of Figure 7 was obtained by a Raman Microscope Horiba T64000, (laser of power 10 mW and wavelength 514 nm, 600 lines/mm grating 300 s acquisition time and 10 accumulations). The spectra of Figure 8 was obtained by the Microscope Raman Dilor XY (1800 lines/mm grating, 300 s acquisition time, 8 accumulations and was used a 514 nm laser of 27 mW). No baseline was fitted. Note that the Raman band at 3595 cm⁻¹ is significant only in the C axis of prasiolite K.

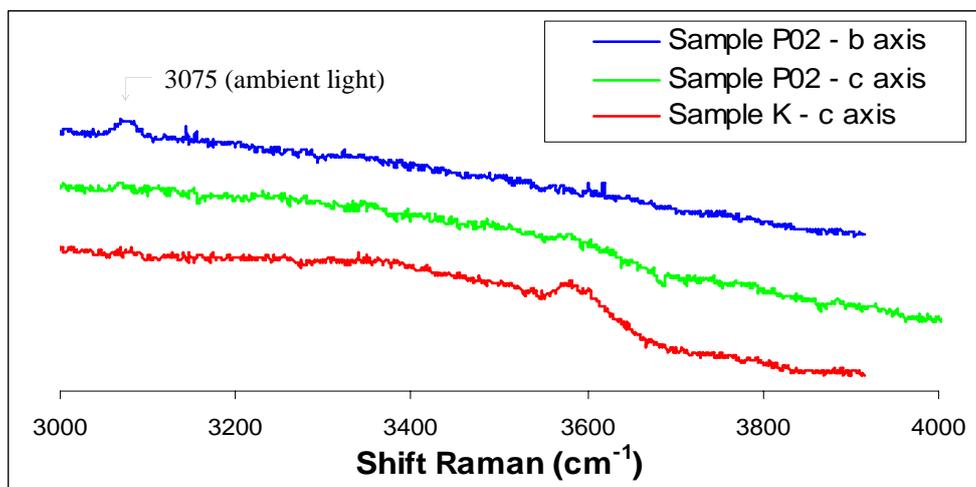


Figure 7: Raman shift of sample K and reference P02 for different sample orientations.

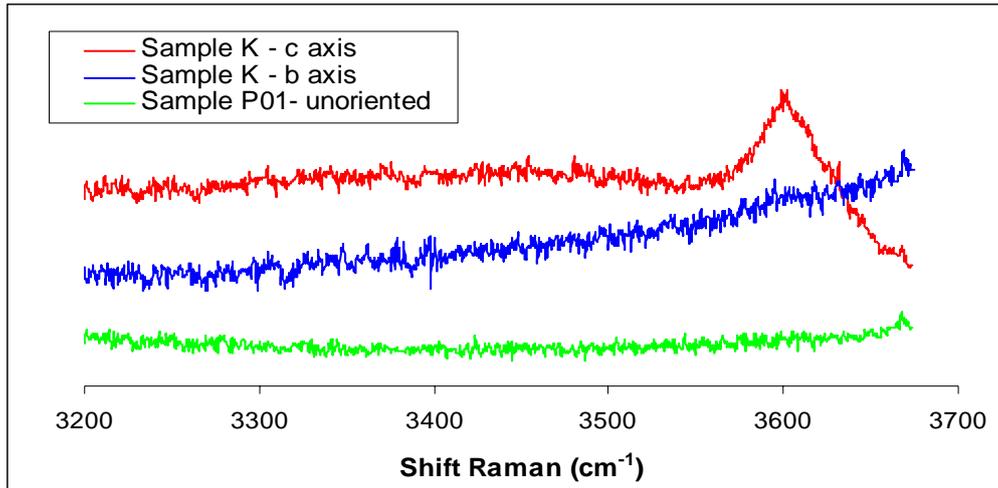


Figure 8: Raman shift of sample K and reference P01 for different sample orientations.

The fluorescence of certain samples generated a great experimental difficulty, especially in the Raman spectrum obtained with such a long time of acquisition. Further tests were performed using the laser of wavelength 633 nm and 785 nm to avoid the fluorescence, but we didn't find any result in the range of interest. The samples that were prasiolites in potential showed intense fluorescence, and sample K was the unique in which it was possible to perform in such conditions.

In order to check the presence of the band at 3595 cm^{-1} in the spectrum of amethyst in potential, the sample A was selected for further Raman spectroscopy (Figure 9). The colorless sample A was selected since it has the largest FTIR impurities signals (see Figure 3). Figure 9 was obtained in a Raman Microscope Horiba T64000, grating of 1800 lines/mm, excited by a laser radiation of wavelength 514 nm 9.9 mW of power, acquisition time of 1800 s and 5 accumulations. The baseline was not fitted.

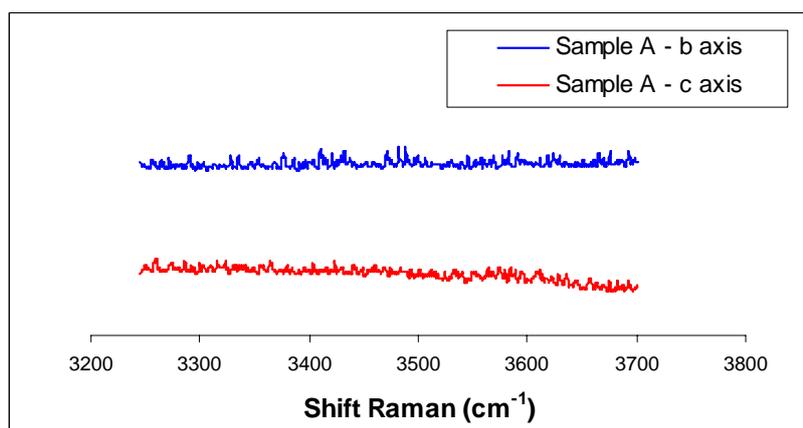


Figure 9: Raman shift of sample A for different sample orientations according to legend.

3. DISCUSSION

Figure 6 shows the difficulty to measure a significant signal with acquisition time of 120 s. Using an acquisition time of 300 s a subtle signal can be appreciated, given by the broad band in the region from 3000 to 3600 cm^{-1} wavenumbers (typical of OH interactions described in the literature). This region of analysis is important to identify the potential of color development in quartz). The excessive noise is a result of a long acquisition time, but it is important to note the Raman shift may be due to impurities in quartz.

Figure 6 is the result of the vibrational behavior of sample K by FTIR and Raman analysis. The band in 3595 cm^{-1} is common on all prasiolites and amethysts FTIR signatures. This band could be measured by both techniques, but it didn't appear in the b axis Raman spectrum. These bands also appeared in the Raman spectra of Figures 7 and 8. Neither references P01 and P02 exhibited this band in any direction, indicating that colorless quartz with no potential for color development may not exhibit this band. Therefore, this mode of vibration at wavenumber 3595 cm^{-1} can be an active mode in both Raman and IR, but it has a directional character in Raman spectroscopy. It would be necessary to perform further tests on other prasiolites to check if it is recurrent in these samples, as we expect. It is certain that amethyst A has lower FTIR absorbance at 3595 cm^{-1} than prasiolite K, but after 1800 s acquisition time, some Raman signal should be expected. It was not observed in Figure 9.

Figure 8 shows some of the most important measurements. It allows us to conclude that the Raman band in 3595 cm^{-1} is probably an active mode of sample K, and not a misinterpretation of noisy measurements. This band is more defined because this system has a 27 mW laser, more powerful than the previous one. The increased laser power results in a considerable increase in Raman scattering with no significant changes in the noise level, since much of the noise is not related to intensity laser.

Measurements of the same sample K were repeated on three Raman devices, and the same band was found in 10 measurements along the C axis with a confidence range (3595,7 \pm 3,4) cm^{-1} . This is a large error due to inaccuracies and noisy measurements.

The positioning of samples relative to the crystallographic orientation was approximated. This may explain the slight variations of the intensity band in 3595 cm^{-1} on some b axis measurements of the same sample.

4. CONCLUSION

With the technology currently available, Raman spectroscopy is little sensitive to chromophore impurities present in colorless quartz that can be activated by ionizing radiation. More studies should be done focusing on this goal, however, the intention to use this technique in the field with the aid of a portable Raman, is still impractical. Measurements must be made under very special conditions and sensitive handsets are not yet available on the market.

The band in 3595 cm^{-1} is common in all prasiolites and amethysts FTIR signatures. It has been reported on Raman spectra of a prasiolite under special conditions like high power depolarized laser, long acquisition time, and greater number of accumulations. This band has not been observed on the colorless quartz used as reference. The vibration that causes the 3595 cm^{-1} band can be an active mode in both Raman and IR spectroscopy, but it is of directional nature in Raman, as it has only been observed when the laser stimulated the c axis of the prasiolite. It would be necessary to perform further tests on other prasiolites and amethysts to check if it is recurrent in these samples as we expect. This band is not expected to be found in other varieties of quartz, still this needs to be confirmed by further studies.

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