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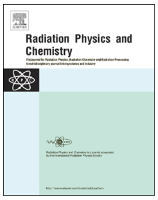

Spectroscopic study of natural quartz samples

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HIGHLIGHTS

- Spectroscopic characterization of natural amethyst, citrine, and prasiolite samples.
- Gamma radiation had a great effect on the color of amethyst and citrine samples.
- The coloration of citrine was not affected by UV radiation.
- Resonance lines observed in EPR spectra of some samples were associated to Fe^{3+}.
- Broad resonance signal observed in EPR spectra of citrine samples.

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ABSTRACT

In this work we performed a spectroscopic characterization of natural amethyst, citrine, and prasiolite samples from different localities. These materials were examined by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV–visible spectroscopy (UV–vis), electron paramagnetic resonance (EPR), and inductively coupled plasma atomic emission spectrometry (ICP-AES). Samples were used in this study in as-received, gamma-irradiated, UV-irradiated, and heat-treated conditions. We observed the changes in the FTIR, UV–vis, and EPR spectra of these samples as a function of the condition they were analyzed. We noticed that gamma radiation had a great effect on the color of amethyst and citrine samples used in this work. It was observed that light colored samples showed a deepening of their colors upon gamma-irradiation and a bleaching upon heat treatment at 450 °C. However, we observed that gamma radiation had a slight effect on the color of citrine. UV-irradiations revealed that the coloration of both amethyst and prasiolite can be bleached by UV radiation. On the other hand, the color of citrine was not affected by UV radiation.

1. Introduction

According to Klein and Hurlburt (1993), quartz is one of the most abundant minerals in the Earth's crust. It is well established that this material show a SiO_4 tetrahedron as its basic structural unit. It belongs to a class of materials known as tectosilicates where the oxygen atoms at the corners of each SiO_4 tetrahedron are shared with adjacent tetrahedra (Klein, 2002). Quartz has been used in many fields, including dating, dosimetry, and electronics (Bahadur, 1989; MacKeever, 2006; Sawakuchi and Okuno, 2004). It is also worth highlighting the use of this material in jewelry (Nassau, 1978, 1984; Lameiras, 2012).

Iron and aluminum are usually observed as impurities in both natural and cultured quartz. They may occupy either the silicon site or an interstitial site in the quartz lattice. Since both iron and aluminum are trivalent whereas silicon is tetravalent, the crystalline defect created when they substitute for silicon must be charge balanced by a positive-charged entity. Examples of ions that can play a charge compensation role in quartz are H^+, Li^+, and Na^+ (Halliburton et al., 1981, Hantehzadeh et al., 1990). In addition, holes created during quartz irradiation can also act as charge compensators. According to Halliburton et al. (1981), because of the strong Coulombic attraction between the substitutional atoms and charge compensators, they are usually present at adjacent sites.

Amethyst is a purple variety of α-quartz whose color has been ascribed to iron impurities (Cohen and Hasan, 1974; Cohen, 1975; Cortezão and Blak 1998; Lehmann, 1975). However, its color is not related solely to these impurities. It is well established that the

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exposure of this material to ionizing radiation is necessary to the development of the purple color (Balitsky et al., 2000; Hutton and Troup, 1966). Cultured amethyst crystals are usually obtained by exposing Fe^{3+}-doped quartz samples to ionizing radiation (Keilson et al. 1987; Tsinober and Chentsova, 1959). Rossman (1994) reported that the purple coloration is observed only in samples where specific sites are occupied by Fe^{3+} ions.

Prasiolite is a green variety of α-quartz. It is also known as green quartz (Rossman, 1994). Neumann and Schmetzer (1984) reported that prasiolite crystals can be obtained by heat treating amethyst samples. The coloration of this material has been ascribed to Fe^{2+} at distorted octahedral sites (Lehmann and Bambauer, 1973). However, this mechanism is not well understood. Since prasiolite crystals usually show light colors, they are commonly irradiated with gamma rays in attempting to obtain samples with deeper colors. Cultured prasiolite crystals have been prepared in stainless steel autoclaves containing either K_2CO_3 or NH_4F aqueous solutions (Balitsky et al., 1975; Khadzhi et al., 1975). According to Chentsova and Tsinober (1966), Fe^{2+} ions released during autoclave corrosion play a key role in the color formation mechanism of cultured prasiolite.

Citrine is a variety of quartz exhibiting colors ranging from yellow to orange (Rossman, 1994). It is usually obtained by heat treating amethyst at temperatures about 500 °C. It is well established that this process is generally irreversible (Pinto et al., 2011). Lehmann and Moore (1966) reported that the concentration of interstitial Fe^{3+}-related defects increases during the heat treatment that transforms amethyst into citrine. They suggested that the color of citrine is associated to the precipitation of iron particles in the quartz lattice, and to the following charge transfer reaction:

$$O^{2-} + Fe_i^{3+} \leftrightarrow O^- + Fe_i^{2+}, \tag{1}$$

where Fe_i represents an Fe ion at an interstitial site. According to Stock and Lehmann (1977), the size of these iron particles is about 100 nm.

In this work we performed a structural characterization of natural amethyst, citrine, and prasiolite samples from different localities. These materials were examined by X-ray powder diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), UV-visible spectroscopy (UV–vis), electron paramagnetic resonance (EPR), and inductively coupled plasma atomic emission spectrometry (ICP-AES). Samples were used in this work in as-received, gamma-irradiated, UV-irradiated, and heat-treated conditions.

2. Materials and methods

In this work we used natural amethyst, prasiolite, and citrine samples from different localities. The chemical composition of these materials was evaluated by ICP-AES, using a Perkin Elmer ICP Optima 3000. The digestion procedure used in the preparation of samples for ICP-AES is better described elsewhere (Lameiras et al., 2009). XRD was performed in a Philips-PANalytical PW17-10 diffractometer, using Cu*K*α radiation and operating at 40 kV and 30 mA. XRD patterns were taken in the angle range from 10° to 80° (2θ), using a 0.06 °/min scan speed. The JCPDS file number 33-1161 was used as reference in the XRD tests. XRD was carried out to assure that the samples used in this work were quartz crystals.

Thin slabs of about 1 mm thickness were cut from the samples using a water-cooled low-speed ISOMET diamond saw (Buehler Ltd.). Since the color, especially in amethyst, is usually unequally distributed within the crystals, samples were cut from a given colored sector. Samples were cut in slices (1 cm × 1 cm) with the *c*-axis perpendicular to the slab plane. Next, they were ground, polished using a diamond paste of 1 μm grain size, washed with detergent, and rinsed with deionized water. Finally, they were placed in an ultrasonic bath with acetone and dried under hot air. These slabs were used in FTIR, UV–vis, and EPR tests.

Samples were used in this study in as-received, gamma-irradiated, UV-irradiated, and heat-treated conditions. It is important mentioning that the as-received amethyst and prasiolite samples showed pale colors. After gamma-irradiation most of them exhibited deep colors. The gamma-irradiation step was performed in a Cobalt-60 Nordion GB-127 panoramic dry gamma irradiator, for dosis ranging from 100 kGy to 1200 kGy. The temperature in the irradiation room was about 60 °C. The dose rate was not controlled, but it ranged from 0.5 kGy/h to 20 kGy/h. The heat treatment step of amethyst and prasiolite samples was performed in air, using a Lindberg/Blue furnace and cooling/heating rates of 10 °C/min. Samples were kept at 450 °C for one hour. UV-irradiation tests were carried out using slabs placed at a distance of about 20 cm from a 5000 W iron iodide lamp. Samples were exposed to UV radiation for times ranging from 5 min to 60 min. In order to keep the temperature of the samples below 50 °C, they were air ventilated during this step.

Since the infrared bands of quartz are thermally sensitive (Bahadur, 1998), the FTIR tests were performed at −196 °C using an ABB Bomem MB102 spectrometer and a Specac cryostat. The FTIR spectra were taken in the spectral range from 3700 cm^{-1} to 2600 cm^{-1}, using a resolution of 1 cm^{-1} and 128 scans. The band at 2677 cm^{-1} was used as reference in these tests because it has been related to Si–O bonds (Lameiras, 2012). UV–vis spectra were taken in the spectral range from 200 nm to 800 nm, using a Shimadzu UV-2401PC spectrometer and a resolution of 0.1 nm. The absorption band at 200 nm was used as reference in these tests. EPR was carried out using a homemade spectrometer composed by a 500 mW klystron (Varian), a commercial resonance cavity (Bruker) operating at X-band (9.39 GHz), and an electromagnet with maximum field amplitude of 800 mT. The EPR spectra were taken at room temperature and recorded as the first derivative of the absorption curve. These tests were performed for samples in crystalline and powdered conditions.

3. Results

XRD tests revealed that the samples used in this work were α-quartz crystals of high purity (content above 98%). The chemical composition of these samples is reported elsewhere (Lameiras et al., 2009). We observed that citrine and amethyst samples showed high concentrations of iron, usually above 20 ppm. On the other hand, prasiolite samples exhibited significant concentrations of aluminum, sodium, and potassium.

Fig. 1 depicts FTIR spectra of quartz samples used in this work. The broad bands centered at about 3200 cm^{-1} and 3300 cm^{-1} are related to Si–O bonds (Halliburton et al., 1981). The features at 3306 cm^{-1}, 3366 cm^{-1}, and 3585 cm^{-1} are ascribed to $[Al_{Si}O_4/H_i^+]^0$ centers, where Al_{Si} represents an aluminum ion at a silicon site (Kats, 1962; Götte et al., 2011). In this defect substitutional aluminum is charge-balanced by H^+. The band at 3436 cm^{-1} is related to Na_i–OH centers (Kats, 1962). In these defects the interstitial alkali ion is charge-balanced by a hydroxyl group. The band at 3545 cm^{-1} is associated to the negative rhombohedron growth sector of quartz (Karampelas et al., 2011). According to Karampelas et al. (2005), this feature is usually observed in natural quartz and rarely noticed in cultured quartz. The band at 3595 cm^{-1} is ascribed to the presence of boron in the quartz lattice (Müller and Koch-Müller, 2009; Staats and Kopp, 1974; Thomas et al., 2009). As far as we know, the features at 3349 cm^{-1}, 3393 cm^{-1}, and 3580 cm^{-1} have not been related to specific hydroxyl-related centers.