

FTIR study of aquamarines after gamma irradiation, heat treatment and electrodiffusion

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Abstract

Beryl, $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$, is a natural gemstone with many colors. Some of these colors can be induced or modified by exposure to ionizing radiation, by heating, and maybe by electrodiffusion. Small contents of chromophore chemical elements are related to the colors of beryl, like iron, chromium, vanadium, manganese, and others. There is great interest in relation to methods of improving or inducing colors in beryl. There is evidence that infrared spectroscopy (FTIR) can contribute to foresee beryl behavior submitted to procedures for color change. It was observed that electrodiffusion with or without contaminant ions did not alter the FTIR spectrum of aquamarines, unlike heat treatment. Green samples have a higher content of type I water molecules, whereas blue samples have a higher content of type II water molecules. Significant changes in FTIR spectra of aquamarines were observed only in green samples after exposure to gamma rays or to heat. The vanishing of the band at 3633 cm^{-1} may be related to the position of Na^+ ion in the crystal lattice of beryl.

Keywords: beryl, aquamarine, gamma rays, electrodiffusion, heating.

1. Introduction

Aquamarine is a variety of blue or blue-green beryl. Its color is due to the presence of Fe^{2+} ion. The content of Fe^{2+} is related to the different blue hues (Polli, 2006a), (Nassau, 2001). If there is also Fe^{3+} , the sample may be light greenish. Most aquamarine samples on the market have a blue hue obtained by color enhancement procedures. Exposure to ionizing radiation and heating are procedures accepted by the market to enhance color because they do not change the original chemical composition of the gemstones. Ionizing radiation

causes Fe^{2+} oxidation to Fe^{3+} and heating can reverse this process. Changing the concentration of these ions in specific sites in the crystal lattice can produce the colors blue, green, yellow, or also a colorless sample.

The color of beryl has great influence on its market value. The color enhancement of beryl by exposure to ionizing radiation can add value to the sample, but not in every case. The same is true for heating. In addition, traders of gemstones expect that the color enhancement procedures produce stable colors.

Concerning beryl, this is very important, because exposure to ionizing radiation can induce a deep blue hue in some samples that vanishes by exposition to visible light. The infrared spectroscopy (FTIR) can help understand these behaviors. On the other hand, electrodiffusion can help understand FTIR spectra by controlled introduction of chromophore ions in beryl crystal lattice.

The objective of this study was to observe the changes in FTIR spectra of beryl samples submitted to electrodiffusion, heating, and gamma irradiation.

2. Materials and methods

Beryl samples from northeast of Minas Gerais were provided by customers of the gamma irradiation facility of CDTN/CNEN. In order to compare the results of this study with the ones of Chen *et al.* (2010), colorless or clear greenish or blueish samples (aquamarine) were used. The samples were cut in a plane perpendicular to the c-axis. A IsoMet precision cutter with a dia-

mond wafering blade were employed. The faces perpendicular to the c-axis were polished with diamond paste of $1\text{ }\mu\text{m}$ and $0.25\text{ }\mu\text{m}$. From each crystal, three to five samples of $6.0 \times 6.0 \times 3.0\text{ mm}$ were obtained. Ten samples of greenish aquamarine and three samples of blueish aquamarine were selected.

The experimental setup for electrodiffusion adapted from Chen *et*

al. (2010) was made of a cylindrical oven, where a quartz tube with the sample holder was introduced (Figure 1). The cathode and anode were made of stainless steel and tungsten, respectively. An alumina tube was used to support the electrodes. The assembly was placed in the center of the oven. The temperature was controlled by an oven controller.

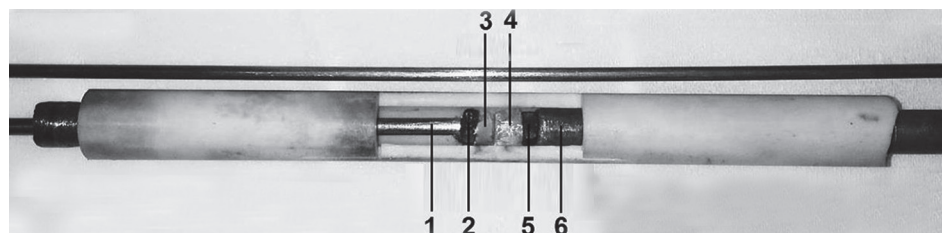


Figure 1

Experimental setup for electrodiffusion - Sample holder: anode (1), graphite pellet (2), salt with the contaminant ion (3), aquamarine sample (4), graphite sample (5), cathode (6).

In the experimental setup (Figure 2), the voltage was supplied by a stabilized DC voltage source, adjustable

from 250 to 5000 V. The voltage was transferred to the sample by means of alligator clips electrical connectors

plugged on the outside structure to avoid damages due to heating.

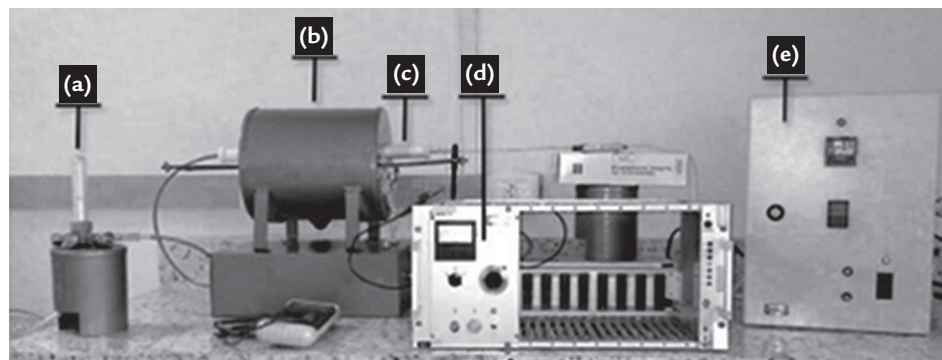


Figure 2

Experimental setup for electrodiffusion: a) nitrogen flow controller, b) cylindrical oven, c) sample holder, d) voltage source, and e) oven controller.

The samples were put in contact on one face with a pellet of an ion donator salt (NaCl , FeCl_3 , MnCl_2). A graphite pellet was put in each side of the sample-salt pellet set. Then, this assembly was placed between the electrodes of the sample holder. The temperature in all experiments was 600°C during six hours, with a heating rate of 10°C per minute. The voltage varied from 1500 V to 3000 V. An inert atmosphere was maintained in the alumina tube by nitrogen flow.

In addition, two experiments were

also carried out in samples of the same crystal. In the first one, the same conditions for electrodiffusion were used, but without the pellets of ion donator salts. In the second one, the voltage was also switched off, being in this case only a heating of the sample.

The samples were irradiated in a MDS Nordion IR-214 series, GB-127 panoramic, multipurpose gamma irradiator, with a ^{60}Co gamma rays source to a dose of 4000 kGy.

FTIR spectra were acquired in eight

samples of greenish aquamarine and in two samples of blueish aquamarine, at room temperature, before and after electrodiffusion and heating. The samples were pulverized by hand in an alumina grail and pistil, and dispersed in KBr. A MB102 ABB Bomem Inc. spectrometer was used, from 400 cm^{-1} to 7000 cm^{-1} , with 16 scans and 4 cm^{-1} resolution. According to Polli (2006a) and Wood and Nassau (1968), the main stretching vibrations of type I and type II of H_2O molecules are in the $3800 - 3400\text{ cm}^{-1}$ interval.

3. Results and discussion

In this study, a colored sample similar to the one reported by Chen *et al.* (2010) was obtained. The thickness of the yellowish layer in the greenish samples after electrodiffusion with no ion donator salt was not measured. But this layer could be easily removed with water-wetted paper towel, showing that it is superficial and external to the sample.

According to Anderson (2006) and Polli *et al.* (2006b), the chromophore ions in greenish aquamarine are Fe^{2+} and Fe^{3+} . In order to increase the concentration of iron ions in beryl, the electrodiffusion was carried out at 600°C , heating rate of 10°C per minute, 2000V voltage, 200 L/h N_2 flowing rate, FeCl_3 as Fe^{3+} ion donator salt. The same procedure was carried out for MnCl_2 , because Mn^{2+} ions are chromophore ions in pink beryl (morganite). In both cases a colored layer could be

observed on the surface of the samples that could be easily removed. It could be an indication that the chromophore ions could not diffuse into a significant volume of the samples.

The channels parallel to the c-axis of the beryl crystal lattice may contain alkaline ions, like Na^+ . According to Anderson (2006 and 2013), these ions can have influence on the orientation of H_2O molecules that are also in these channels. Electrodiffusion experiments were carried out with NaCl and KCl as, respectively, Na^+ and K^+ donors to observe changes in beryl. In both cases the greenish samples became colorless, possibly as a result of reduction of Fe^{3+} to Fe^{2+} caused by heating.

The Fe^{2+} ions, both in tetrahedral or octahedral positions, is an electron hole precursor (Ibragimova *et al.*, 2009; Anderson, 2013). During irradiation, Fe^{2+}

transforms into Fe^{3+} , creating an electron hole. The ejected electron is trapped in the crystal lattice as an electron center. When the crystal is heated, the electron is released from the trap and captured by Fe^{3+} , which is converted into Fe^{2+} .

Figure 3 shows FTIR spectra of blueish aquamarine samples as-received (natural), after heating, and after irradiation. No significant changes could be observed in this spectrum region. But Figure 4 shows that it is not the case for the greenish aquamarine samples. In summary, one can observe: 1) heating causes the vanishing of the band at 3663 cm^{-1} , which is related to a combination of absorptions of type II H_2O molecules and OH-Na (Aurisicchio *et al.*, 1994); 2) the band at 3663 cm^{-1} grows with irradiation; 3) heating of irradiated samples causes the vanishing of the band at 3663 cm^{-1} .

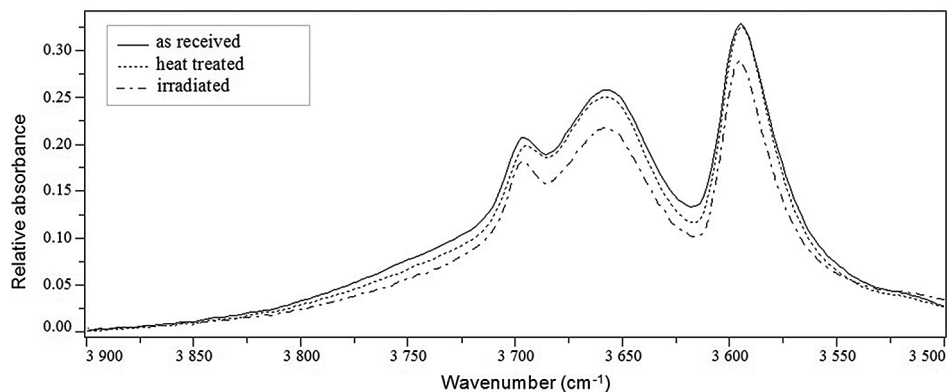


Figure 3
FTIR spectra of blueish aquamarine samples as-received (natural), after heating, and after gamma irradiation to 4000 kGy.

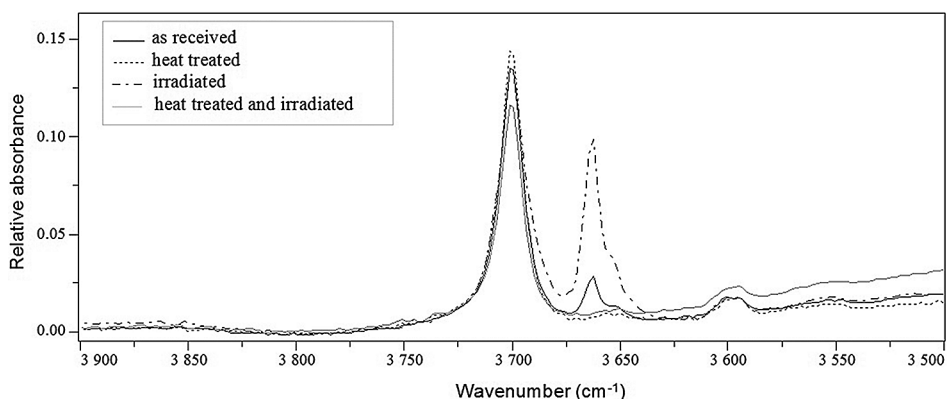


Figure 4
FTIR spectra of greenish aquamarine samples as-received (natural), after heating, after gamma irradiation to 4000 kGy, and after gamma irradiation and heating.

When the channels along the *c*-axis in beryl crystal lattice are free from alkalis, H₂O molecules are preferably oriented as type I. When the channels are rich in Na⁺ ions, H₂O molecules are preferably oriented as type II (Wood and Nassau, 1968). Beyond the vibrations related to both types of H₂O molecules, Aurisicchio *et al.* (1994) also attributed the band at 3658 cm⁻¹ to OH-Na. From EPR (electronic paramagnetic resonance) studies, Anderson (2006) reported that Na⁺ ions can occupy the position 2b, proposed by Aurisicchio

et al. (1994), as well as the position 2a (Figure 5). The position 2a in the beryl channel has enough space to contain an Na⁺ ion together with a type I H₂O molecule.

The cause of the yellowish component in greenish aquamarine is the Fe³⁺ ion as a substitute for Al³⁺ in octahedral positions. Both, Fe³⁺ and Al³⁺, have the oxidation state, so that charge equilibrium is maintained. Heating at 600 °C causes the reduction of Fe³⁺ ions to Fe²⁺ at an octahedral position, causing charge imbalance. Since Na⁺ ions can be at

positions 2a and 2b (Anderson, 2006), it can be a charge compensator for Fe²⁺ migrating from position 2a to position 2b. As a result, type I H₂O molecules would shift to type II H₂O molecules. The results of this study corroborate this hypothesis. Natural greenish aquamarine has a small band at 3663 cm⁻¹, related to type I H₂O molecules. It grows with irradiation, caused by oxidation of Fe²⁺ to Fe³⁺, dislocation of Na⁺ from position 2a to position 2b, and the shifting of type I H₂O molecules to type II, as shown in Figure 5.

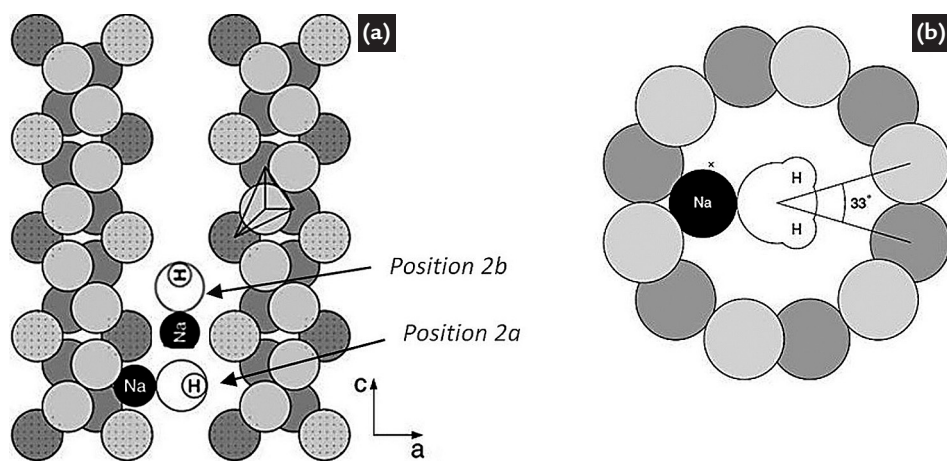


Figure 5
Alkalies and water representation in the channels of beryl lattice: a) beryl channel with Na⁺ ion at position 2a interacting with type I H₂O molecule, and Na⁺ ion at position 2b interacting with type II H₂O molecule; b) Na⁺ at position 2a seen from above a plane perpendicular to the *c*-axis (001). Adapted from Anderson (2006).

The 3663 cm⁻¹ band of natural or irradiated greenish aquamarine samples decreased with heating, probably due to

dislocation of Na⁺ ions from position 2b to 2a. The blueish aquamarine samples did not show significant changes in

FTIR spectra. The highest concentration of type II H₂O molecules in these samples are related to higher concentra-

tion of alkaline ions in the channels, Graça (2001). If they have large ionic radii, the dislocation of Na⁺ may be

hindered. By heating, the blueish sample (natural or irradiated) the yellowish component is lost, but the Na⁺ ions can-

not dislocate to position 2a to balance the Fe²⁺ charge in the octahedral positions, the 3663 cm⁻¹ band is unchanged.

4. Conclusions

Electrodiffusion carried out under the conditions of this study did not change FTIR spectra of blueish or greenish aquamarine samples. The changes observed in

color and in FTIR spectra were caused by heating.

Significant changes in FTIR spectra were observed only in greenish samples,

either by gamma irradiation or heating. The decrease of the band at 3663 cm⁻¹ may be related to the position of Na⁺ ions in the beryl channel along the c-axis.

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