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Gamma-ray effect on natural quartz gem crystals' quality from Qazvin and Astane regions, Iran

Razieh Rezaee*[a], Seyed Amirhosein Feghhi[b], Fariborz Masoudi[a]

[a] Department of Geology, Faculty of Earth Sciences, Shahid Beheshti University, Iran
[b] Department of Radiation Application, Faculty of Nuclear Engineering, Shahid Beheshti University, Iran

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*corresponding author.
E-mail address:
rezaeerazieh.r@gmail.com
(R. Rezaee)

ABSTRACT

In this study, irradiation treatment was examined on colorless and clear quartz crystals collected from east of Qazvin (EQ) and southwest of Astane (SWA) regions in Iran. EQ crystals up to 3 cm were found in the geodes in andesite and trachyandesite, while idiomorphic crystals up to 2 cm from SWA formed in cavities and vugs in rhyodacitic host rocks. Crystals of both locations were exposed to gamma rays under the same conditions in steps of 100 kGy, 200 kGy and 300 kGy. No specific color change was observed for EQ crystals, while colorless SWA samples completely turned into dark gray or smoky gray from 100 kGy onwards. Comparing chemical analysis (ICP_MS) of samples revealed that SWA crystals contain more impurities with significantly higher Al. Representative Al contents in EQ and SWA samples are 322 ppm and 3378 ppm respectively. Data from Raman and infrared spectroscopy structural analyses, show similarities between studied samples from both regions. Formation of smoky quartz after radiation is related to color center defects. Field evidence reveal the direct effect of hydrothermal fluids and vapors related to Astane granitic intrusions on country rocks in the aureole, in forming colorless quartz crystals with high concentrations of aluminum impurities substituting Si.

1. Introduction

The use of radiation and subsequent heat treatment to change the color of minerals is a widespread method to increase the value of gem materials (e.g. Leal, 2007; McClure et al., 2010). During the last decades, the use of ^{60}Co radiation has shown effective results on color modification of quartz. Quartz, in the stable crystallized form of silica, has many natural gem varieties. The two common types are violet amethyst and citrine with its yellowish brown shades of color. Commercial irradiation units for gemstone treatment exist worldwide. It is likely that many colorful quartz gemstones are produced by radiation methods (Enokihara et al., 2012). Quartz or more precisely α-quartz is a tectosilicate with three-dimensional arrangements of polymerized tetrahedrons of SiO_4. It is stable in normal conditions up to 573°C. The quartz crystal can build right-handed or left-handed crystal forms. Under most growth conditions, some twin intergrowth between these two forms will occur, giving rise to growth defects (Enokihara et al., 2012).

The small ionic size of silicon does not permit substitution by most elements with the exception of mainly trivalent iron, alumina, phosphorous and germanium. Quartz is therefore, a quite pure mineral and as shown by Iwasaki et al. (1991) and Guzzo (1992), may contain impurities. These impurities can be classified as included material in the form of mineral matter (e.g. Klemme et al., 2018) or fluid inclusions and as structural units. Those structural impurities, mainly responsible for the color centers, may be substitutional or interstitial. Fe^{3+}, Al^{3+}, OH^- and H_2O molecules are substitutional and Na^+, Li^+ and H_3O^+ are interstitial units located in the channels of the structure (Enokihara et al., 2012). The most abundant element, which is observed in the form of an impurity in quartz, is aluminum (up to 1000 ppm). This is due to the abundance of Al in the Earth's crust and ion radius' near to Si. The present study aims to explore the use of gamma radiation to induce color in quartz crystals with non-identical aluminum content, collected from Qazvin and Astane regions in Iran.

2. Material and Methods

Materials

Clear idiomorphic quartz crystals were collected from an area in East of Qazvin (EQ) and an area in South west of Astane (SWA). Qazvin is located about 150 km west of Tehran. Studied EQ area is between the two cities of Abyek and Qazvin on the north of Tehran- Qazvin highway. The area is a part of the Central Alborz geological zone. Gemstones from silica family, including agate, jasper and geodes are scattered in andesibasalt, trachyandisite and trachyte host rocks. In this study, clear crystals with proper form or shape in geodes were separated and used for treatment. The size of the crystals is no larger than 4 mm. Astane is located in southwest of Arak city. Investigated SWA area is a part of the Astane granitic intrusion, which is located in the Sanandaj-Sirjan metamorphic geological zone. Host rhyodacitic rocks in the aureole are affected by post magmatic volatile alteration. They are clear in prismatic or needle shapes where quartz crystals up to 2 cm in length have crystallized in cavities and vugs. Contamination with iron oxides is common.

Irradiation procedures

The batches of colorless quartz were irradiated in a ^{60}Co source chamber (Gamma Cell-220) at doses of 100, 200 and 300 kGy in the ambient atmosphere and the dose rate of 1.4 Gy/s was determined by Perspex dosimeters.

2.1. Methods of characterization

Ten representative quartz crystals, in their natural state as well as post-irradiation and absorbing the dose of 300 kGy, have been selected for preliminary chemical and spectroscopic characterization. The chemical composition was carried on by routine method of ICP-mass spectroscopy (ICP-Ms), at the Chemical Laboratory of the Zarazma Institute. Ultraviolet-visible and ATR (Attenuated Total Reflectance) infrared spectroscopy from 200 to 4000 nm were characterized at the Physics Department of the Shahid Beheshti University. Raman spectroscopy was performed at the Gemology Laboratory of the Shahid Beheshti Gemology Center.

3. Results and discussion

Irradiation effects

The crystals of both EQ and SWA regions were exposed to gamma rays under the same conditions in steps of 100 kGy, 200 kGy and 300 kGy. No specific color change was observed for EQ crystals; only limited parts of few crystals turned into dark gray, while colorless SWA samples completely turned into dark gray or smoky gray from 100 kGy onwards. Figure 1 shows the crystals of both regions before and after irradiation. To determine the stability of the color produced by the irradiation, those crystals that were irradiated to 300 kGy and completely changed to dark smoky, were heated to a temperature of 150˚C for one hour. After heating, the crystals preserved their dark color.

Chemical analysis

In order to characterize chemical composition of trace elements in crystals, samples are analyzed by ICP_MS method (table 1). Results confirm that the crystal chemistry of the hydrothermal quartz of SWA are mainly dominated by substitution of iron, alumina and hydroxyl or molecular water impurities, consistent with the data shown by Guzzo (1992). No systematic study was undertaken in order to correlate chemical composition to shade and depth of color or evaluate correlation between values of iron and alumina with color (Enokihara et al., 2012). Comparing chemical analysis (ICP_MS) of samples from two investigated regions, reveal that SWA crystals contain more impurities with significantly higher Al. Representative Al contents in EQ and SWA samples are 322 ppm and 3378 ppm respectively (Table 1).

Fig. 1. a) Quartz crystals of the EQ region before irradiation. b) Crystals of the EQ produced by irradiation till 100 kGy. c) Crystals of the EQ produced by irradiation till 200 kGy. d) Crystals of the EQ produced by irradiation till 300 kGy. e) Quartz crystals of the SWA region before irradiation. f) The crystals belonging to the SWA that are completely colored with smoky color (They are irradiated from left to right at 100, 200 and 300 kGy).

Table 1. Representative ICP chemical analysis (in ppm) of studied samples for selected elements.

Element	EQ	SWA	Element	EQ	SWA
Al	322	3378	Ba	<1	58
Na	202	333	Cu	11	25
Mg	105	403	Ca	187	409
Li	1	6	Pb	<1	3
Fe	6852	14438	P	32	45
K	<100	1260	Ni	3	7
Mn	80	122	Sr	<1	1.7
Ti	<10	323	Sn	0.9	2.3

4. Conclusion

4.1. Raman spectroscopy

Raman analysis reports spectrums based on molecular structure of materials and using Raman spectroscopy, many minerals are identified in a short time. The method is completely reliable and confirms the authenticity of other tests of gemology. Nowadays, Raman spectroscopy is a common technique in gemology laboratories, in order to identify the type of gemstone and its treatment. One of the significant advantages of this method is the lack of need for sample preparation. In this study, quartz crystals of both regions were analyzed before and after irradiation using Raman model through TAKRAM P50C0R10 with a laser wavelength of 532 nm and laser power of 0.5 _70 mv.

As shown in Fig2, the Raman quartz spectrum can be divided into three regions:

1. Wavelengths exceeding 1050 and wavelengths of 700-800 cm^{-1}, which are related to Si-O expansion modes.

2. The wavelengths of 350-500 cm^{-1} show the O-Si-O bending modes.

3. Wavelengths less than 300 cm^{-1}, which are related to the Si-O-Si bending and rotating modes (Etchepare et al., 1974).

The peak appearing in 465cm^{-1} for quartz is considered as a fingerprint, and in fact, quartz detection using the Raman spectrum is based on this main peak.

As shown in Figure 2, the Raman spectrum of the Qazvin crystals did not change after irradiation.

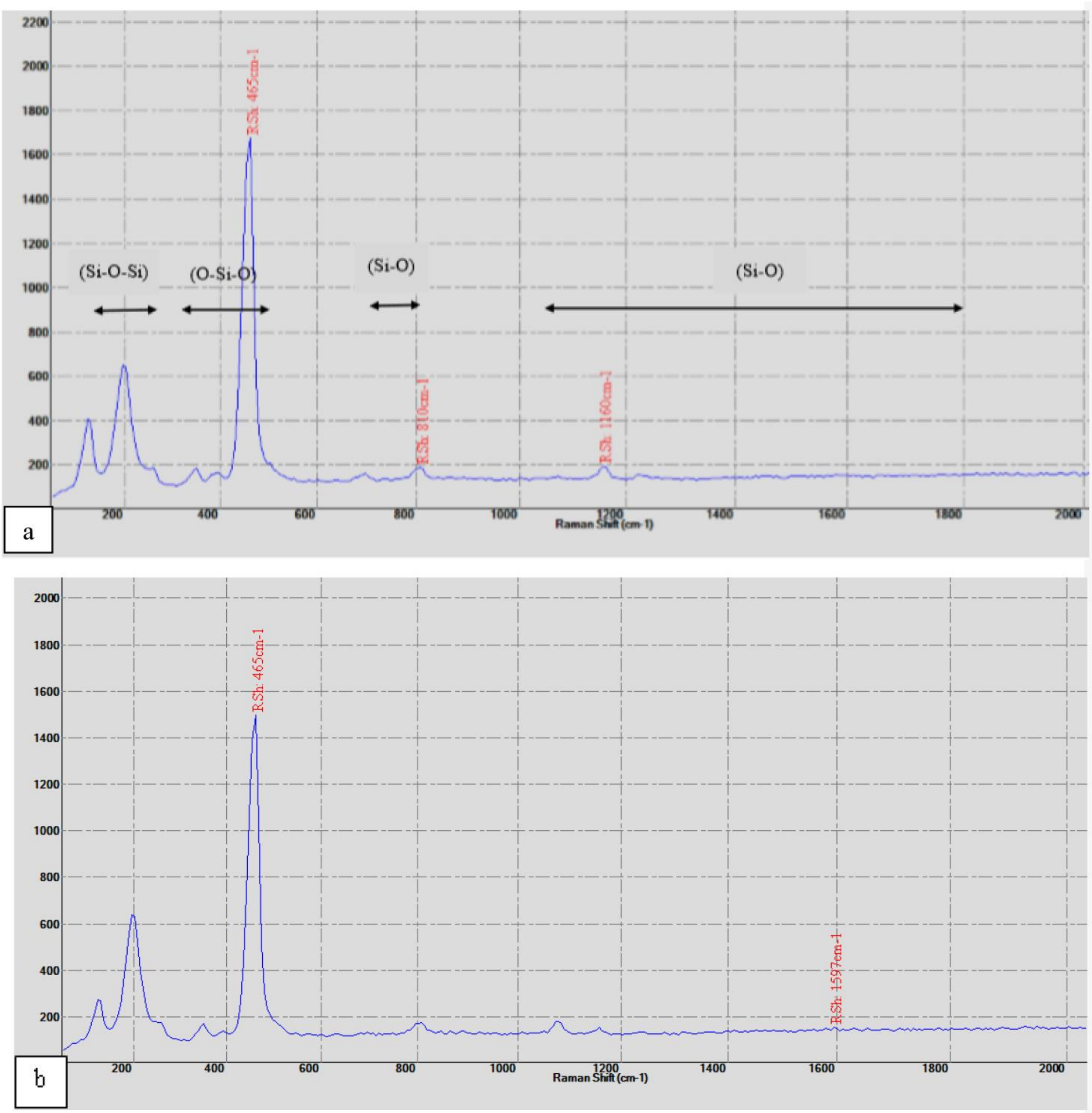

Fig. 2. a) Raman spectrum of quartz from EQ before irradiation. b) Raman spectrum of an irradiated quartz from EQ.

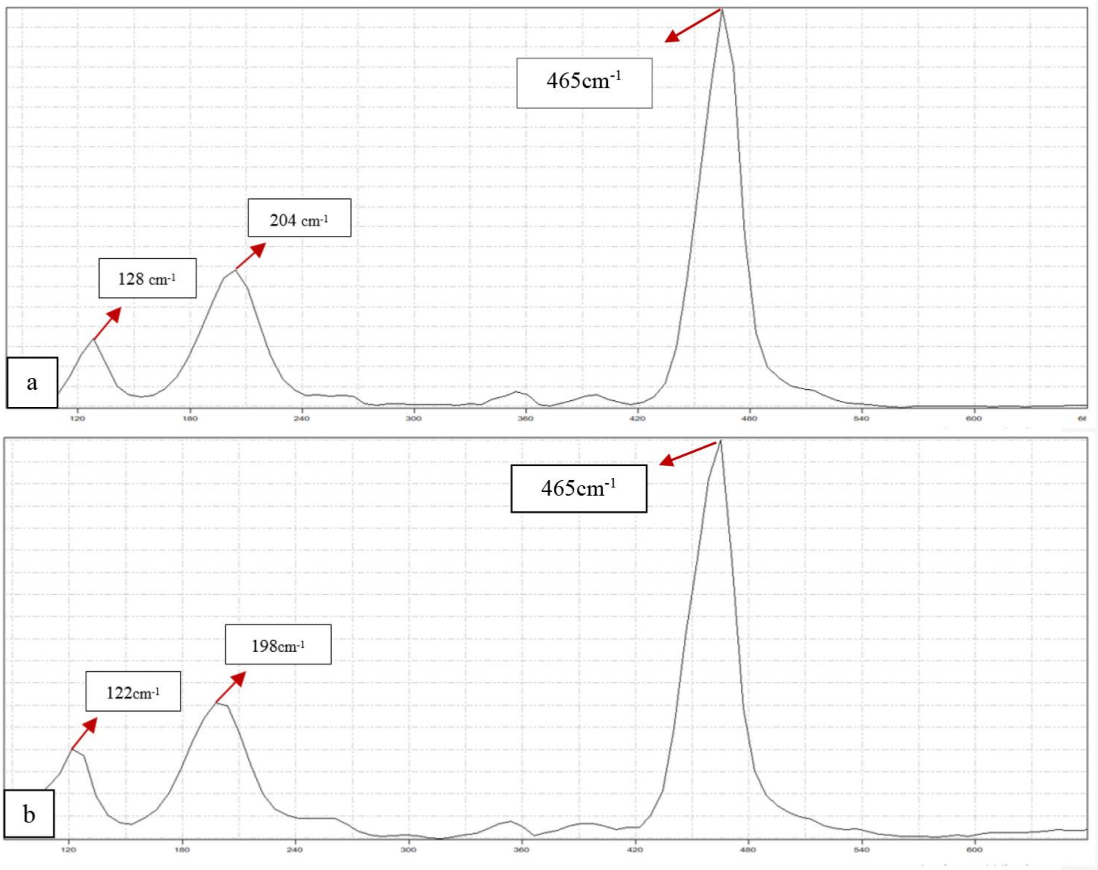

Fig. 3. a) Raman spectrum of quartz from SWA before irradiation. b) Raman spectrum of an irradiated quartz from SWA.

Regarding quartz crystals of the Astane region, the present study reveals that the peak at 128 cm^{-1} and 204 cm^{-1} before irradiation, shifted towards lower wavenumbers deviating by 6 cm^{-1}. However, the peak at 465cm^{-1} remains unchanged (Figure 3).

4.2. UV-VIS and ATR spectroscopy

Figure 4 shows the UV/VIS spectra of the crystals of EQ area. The crystals of Qazvin area show strong absorptions at wavelengths smaller than 300 nm. From the spectroscopic evidences, it appears that the high water content overrides the influences of Fe and Al contained in the samples (Enokihara et al., 2012). This means that the normal color centers related to iron and alumina are masked by the presence of high amounts of molecular water and OH (Aines and Rossman, 1986).

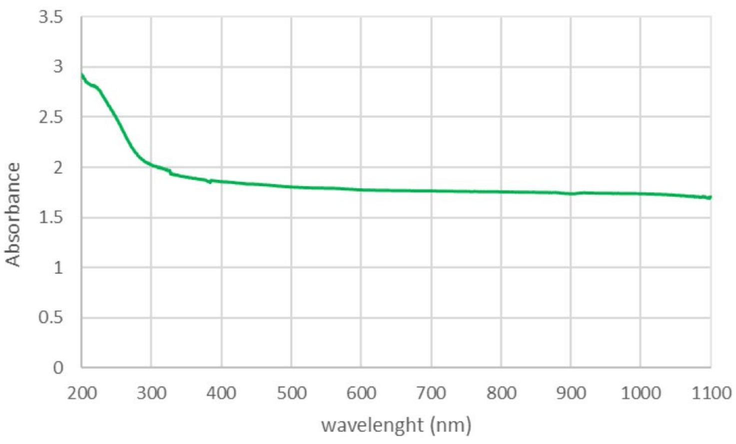

Fig. 4. UV-VIS spectrum of EQ quartz sample before irradiation.

Figure 5 shows the results of the ATR analysis of the crystals of both regions. The wavelengths between 1900 and 2300 show the presence of water and OH in the samples. The spectra obtained from ATR analysis also emphasizes the presence of OH in both quartz regions.

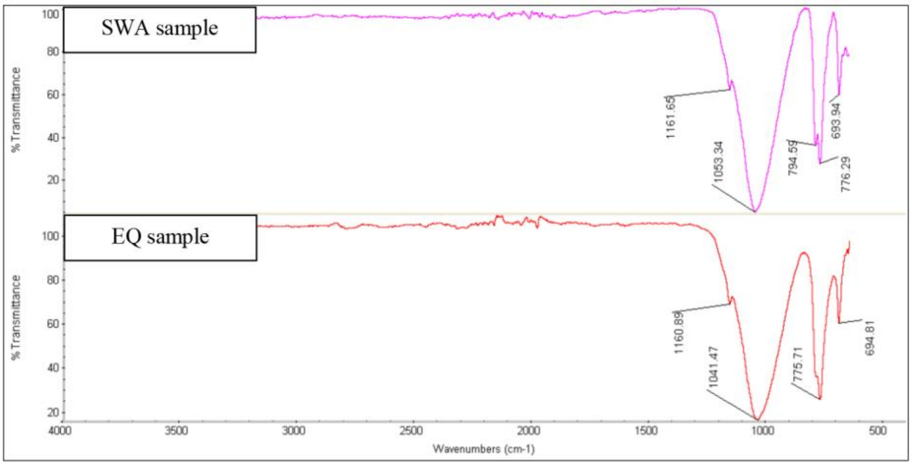

Fig. 5. ATR spectra of both regions before irradiation

4.3. Color Cause

The general theories about the origin of color in gem materials were published by Nassau (1975), Nassau (1978), Loeffler and Burns (1976), Marfunin (1979) and Fritsch (1985). Based on crystal field theory, many colors in gemstones such as amethyst, fluorite and smoky quartz are the result of exposure to high-energy radiation. This can happen by natural radiation or through artificial irradiation in laboratories. Radiation can: 1) change the oxidation state of metal ions and 2) interact with "defects" in the crystal. Color center is the generic term for a defect that causes light absorption (Fritsch and Rossman, 1988). Kittel (1980) provides more details on theoretical approaches to color centers. The concept of color center is best explained through typical example of aluminum ($A1^{3+}$) replacing a small part of the silicon (Si^{4+}) as impurity in quartz. Irradiation can remove an electron from an oxygen atom adjacent to an aluminum ion, creating an intense absorption of light and induce the typical smoky color. Chemical analysis of studied samples, show high enough Al concentration in SWA samples (3378 ppm) to form smoky crystals after radiation based on crystal field theory. However, Al content (322 ppm) in EQ samples is within the range of most natural quartz crystals that contain substitutional Al at the range of several hundred ppm (Nassau, 1978), which is not high enough to absorb light. Furthermore, colorless forms of quartz crystals grow in different geological conditions in the presence of magmatic and metheoric fluids. From the evidence, it is shown that direct hydrothermal fluids and vapors related to Astane granitic intrusion could affect country rocks in the aureole leading to formation of colorless quartz crystals with high concentration of aluminum impurity as substitution of Si. Crystals of SWA area with high Al content change to smoky crystals with radiation dosages of 100 kGy, with no more significant color change in higher radiation dosages. Quartz crystals in EQ area were formed in volcanic terrains, with Al contents in the range of common natural quartz crystals. This content is not high enough for significant color changes even in high radiation dosages (up to 300 kGy).

References

Aines, R.D., Rossman, G.R., 1986. Relationship between radiation damage and trace water in zircon, quartz and topaz. Am Mineral: 71, 1186-1193.

Enokihara, C.T., Guttler, R.A.S., Rela, P.R., Calvo, W.A.P., 2012. “Studies of colored varieties of Brazilian quartz produced by gamma radiation” Presented at the International Meeting on Radiation Processing - IMRP 2011, Montreal, Canada.

Etchepare, J., Merin, M., Smetankine, L., 1974. “Vibrational normal modes of SiO_2. I. α and β quartz”. Chem. Phys: 60, 1874-1876.

Fritsch, E., 1985. La couleur des minkraux et des gemmes, dellxierne partie. Monde el Minbraix: 69, 12-17.

Fritsch, E., Rossman, G.R., 1988. An update on color in gems. Part 2: Color involving multiple atoms and color centers. Gems and Gemology, 24, 3-15.

Guzzo, PL., 1992. Characterization of the structures impurities and defects centers related to Al and OH in natural quartz. Dissertation Mechanical Engineering Department, Campinas University.

Henn, U., Güttler, R.A.S., 2012. Review of some current coloured quartz varieties. Gemmol: 33, 29-43.

Iwasaki, H., Iwasaki, F., Oliveira, V.A., Hummel, D.C., Pasquali, M.A., Guzzo, P.L., Watanabe, N. & Suzuki, C.K., 1991. Impurity content characterization of Brazilian quartz lascas. Japanese journal of applied physics, 30(7), 1489-1495.

Kittel, C., 1980. Introduction to Solid State Physics, 4th ed. John Wiley & Sons, New York.

Klemme, S., Berndt, J., Mavrogonatos, C., Flemetakis, S., Baziotis, I., Voudouris, P., Xydous, S., 2018. On the Color and Genesis of Prase (Green Quartz) and Amethyst from the Island of Serifos, Cyclades. Minerals: 8(11), 487 p.

Leal, A.S., Krambrock, K., Ribeiro, L.G.M., Menezes, M.A.B.C., Vermaercke, P., Sneyers, L., 2007. Study of neutron irradiation-induced colors in Brazilian topaz. Nuclear Instruments and Methods. Physics Research: A 580, 423-426.

Loeffler, B.M., Burns, I.G., 1976. Shedding light on the color of gems and minerals. Americnn Scientist: 64, (6), 636-647.

Marfunin, A.S., 2012. Spectroscopy, luminescence and radiation centers in minerals. Springer Science & Business Media.

McClure, SF., Kane, R.E., Sturman, N., 2010. Gemstone enhancement and its detection in the 2000s. Gems & Gemology: 46, 218-240

Nassau, K., 1978. The origins of color in minerals. American Mineralogist: 63, 219-229.