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Effect of irradiation and thermal annealing on quartz materials luminescence

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Abstract. X-ray and gamma-quanta irradiation of radiation-resistant quartz materials including natural and synthetic quartz crystals and high-purity quartzite causes the luminescence in the ultraviolet range (365 nm), thermally stimulated luminescence and radiofrequency electromagnetic emission. Preliminary radiation and thermal annealing improves luminescence properties of quartz materials.

1. Introduction

Quartz materials are widely used to manufacture various kinds of things including quartz radiodes and epireadies for compound semiconductors which must meet special requirements on defect population and on control over defect modifications under various radiation and/or thermal actions. Imperfection of natural quartz as a mineral is caused by its genetic formation conditions, whereas imperfection of synthetic quartz is represented by its biographic defects as a result of its synthesis. As a rule the purest and most transparent varieties of quartz materials of both the natural and synthetic origin contain few optically –inactive imperfections which can be detected with non-destructive luminescence methods [1, 2].

This paper covers the variation of luminescence properties of quartz materials when being exposed to a thermal and radiation action.

2. Research methodology

Quartz materials were exposed to X-ray radiation (X-ray luminescence) and to heat action at a temperature of up to 400 °C (thermally stimulated luminescence) and then their luminescence spectra in the range of 300...800 nm were studied. The research methodology was the same as common photometric procedures [3, 4]. In addition, a method of synchronous recording of radiofrequency (RF) electromagnetic emission was also used [4-6].

Samples of quartz materials including natural and synthetic quartz and highly-pure quartzite were in a form of thin plates, 10×10×1 mm in size.

3. Experimental results and discussion

When highly-pure synthetic and natural quartz crystals and natural quartzite are exposed to X-ray radiation, a slight glow appears in the range of 620…650 nm (Fig.1, Curve 1). Irradiation of quartz crystals with X-rays or gamma-quanta results in ionization of silicon-oxygen tetrahedron and occurrence of recombination centers represented by oxygen ions. The luminescence recorded in the ultraviolet range and in the range of 630 nm is caused by recombination processes occurring in $[SiO_4]^{3-}$ -hole-centers and on nonbridging oxygen ions (Fig.1, Curve 2), respectively. Thermal pre-treatment of non-irradiated natural quartz samples even at rather low temperatures of 150°C results in drastic increase of the luminous intensity in the ultraviolet range (Fig.1, Curves 2 and 3).

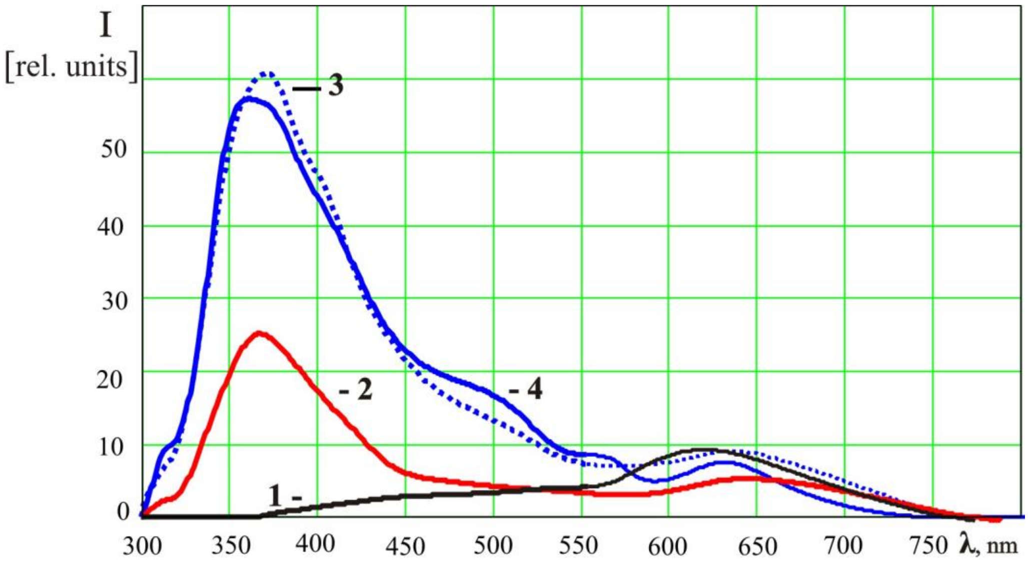

Figure 1. X-ray luminescence spectra of natural quartz crystals: 1 – virgin sample, 2 – irradiated by gamma-quantum, 3 – heated up to 150 °C, 4 – heated up to 400 °C.

Occurrence of thermally-stimulated luminescence (TSL) in crystals is associated with crystal imperfection, radioactive elements impurities and ionizing irradiation of them. The TSL mechanism is well explained by a band theory.

The TSL phenomenon is not observed in synthetic quartz samples. Highly-pure quartzites are characterized with a weak natural thermally-stimulated luminescence in the high-temperature range of 220-235 °C and 285-290 °C [4]. The TSL of natural quartz crystals is conditioned by the mineral formation environment and is widely used to restore the genetic information. In order to stimulate the mineral's "memory", crystals are irradiated with ionizing radiation that causes the induced TSL and significantly extends the TSL applications to solve mineralogy and material engineering practical tasks.

Irradiation of radiation-resistant quartz crystals with X-rays and gamma-quanta does not cause new defects in the crystalline lattice but results in ionization of silicon-oxygen tetrahedron and, probably, OH-groups in the quartz lattice. This also leads to developing various electrically active defects including dislocations, grain boundaries, blocks, point defects and color centers which "trap" electrons and "holes" [4, 5]. Further heating up of quartz crystals is accompanied both with the thermo luminescence and electromagnetic emission in the RF range (Fig.2). The electromagnetic emission is especially intensive in a low temperature range of 50…70 °C.

In nominally pure synthetic quartz crystals the electron-hole color centers are not stable due to a mobile hydrogen ion (proton) present in synthetic quartz crystals as an ion – compensator or formed in them due to ionizing processes; the mobile hydrogen ion, residing next to silicon-oxygen tetrahedra, does not allow creating a stable hole $[SiO_4]^{3-}$ center responsible for TSL in the temperature range of 50…70 °C.

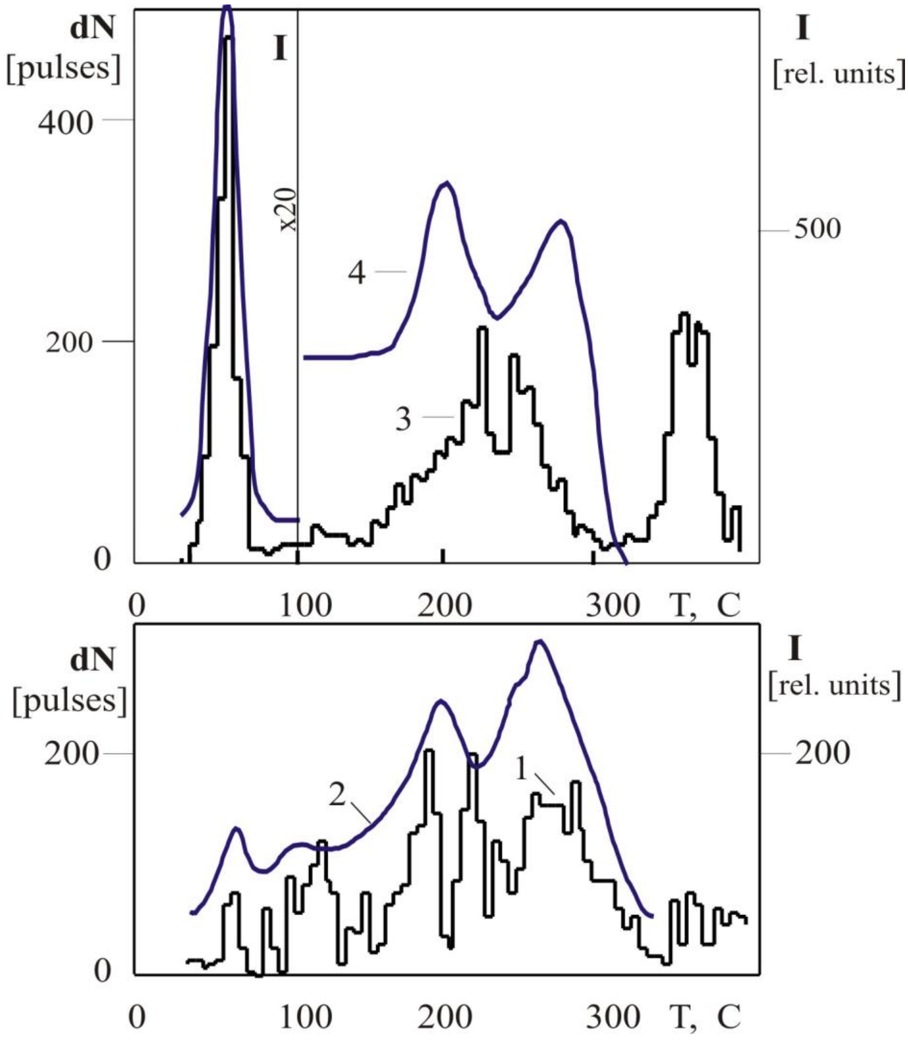

Figure 2. Radiofrequency electromagnetic emission (1, 3) and luminescence (2, 4) occurred in synthetic quartz crystals when being heated and the same dose (4.0×10^3 Gy) irradiated with gamma-quanta of the dose rate of 0,038 Gy/s (1, 2) and 3,6 Gy/s (3, 4).

When quartz crystals are irradiated with a high gamma dose rate of ~ 3,6 Gy/s, unlike the irradiation with gamma-quanta of low dose rate (~0,038 Gy/s), it causes more defects to occur due to high density of stimulation; such extra defects effectively stabilize fast hydrogen ions that results in creating a stable couple of centers, i.e. an electron $[SiO_4]^{5-}$ center and a hole center:

$[SiO_4]^{3-}$: $[SiO_4]^{4-} + e^-\} = [SiO_4]^{5-}$ and $\{[SiO_4]^{4-} + e^+\} = [SiO_4]^{3-}$.

The heat action destroys electron centers that causes the release of electron and, then, its recombination on oxygen ions according to the following scheme:

$$[SiO_4]^{5-} \rightarrow \{[SiO_4]^{4-} + e^-\} + [SiO_4]^{3-} \rightarrow [SiO_4]^{4-} + h\nu \text{ (365 nm) and}$$

$$[SiO_4]^{5-} \rightarrow \{[SiO_4]^{4-} + e^-\} + O^- \text{ (nonbridging)} + h\nu \text{ (630 nm)},$$

This, in its turn, causes the intensive TSL and RF electromagnetic emission in the temperature range of 50…70 °C (Fig.2, Curves 3, 4).

It should be noted that the luminescence intensity in heat-treated samples increased in the high temperature range by 2-3 times with remaining the type of thermal luminescence curve the same, as mentioned in [7]. But a more significant difference of by 20-40 times is observed in the low-temperature luminescence peak at ~ 50…70 °C; moreover, when quartz crystals are thermally annealed, their luminescence intensity at this peak is higher for those crystals which were pre-irradiated than for samples subjected to heat treatment only.

4. Conclusion

The temperature dependences of luminescence and radiofrequency electromagnetic emission can characterize imperfection and electrical micro heterogeneity of quartz materials. Defects in quartz materials are developed during crystallization and various handling treatments and due to external irradiation or thermal actions. A crystal or a mineral, by assimilating external actions and accumulating genetic information, keeps, so to say, the memory about actions and events it has experienced [8].

Irradiation has a significantly effect on the imperfection status of quartz and the degree of such an effect depends on a genetic type of quartz and on pre-heat treatment of quartz materials. When modifying quartz materials with ionizing irradiation, one should take into consideration both the irradiation type and the dose rate. The heat treatment even at lower temperatures of ~ 150 °C results in changes in microdefects and the increase in luminescence sensibilization of quartz materials.

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