STUDY OF COLORED CRYSTALS OF SYNTHETIC QUARTZ

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STUDY OF COLORED CRYSTALS OF SYNTHETIC QUARTZ

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It is known ($^{1-3}$) that, when quartz crystals are grown by the temperature-gradient method from aqueous solutions of K_2CO_3 and Na_2CO_3, with the introduction into the system of pigmenting additives, colored varieties of this mineral—green, brown, and blue—are formed under certain experimental conditions. Green and brown crystals were obtained using aqueous K_2CO_3 solutions in systems enriched with an admixture of iron. At a comparatively low concentration of potash in the solution (up to 5-7%), predominantly brown crystals are formed, while at a higher concentration green ones are formed. Often the green and brown colors are observed in one and the same crystal, with sectorial and zonal polychromy occurring. Blue crystals were synthesized in Na_2CO_3 solutions with the addition to the autoclave of an admixture of cobalt. Analysis of the regularities of the sectorial and zonal distribution of the indicated types of coloration testifies to a close connection of the coloring centers with the so-called nonstructural impurity (^{3}). In the opinion of most investigators, the nonstructural impurity in synthetic quartz is represented by colloidal inclusions of sodium (potassium) silicates captured by the crystal during growth.

In order to clarify the nature of the green, brown, and blue coloration of quartz, we carried out studies of the spectra of electron paramagnetic resonance (e.p.r.) (RE-1301 radiospectrometer), optical absorption (SF-8 spectrophotometer), and also electron microscopy (IEM-6A electron microscope) of colored crystals.

In crystals of brown quartz, the e.p.r. spectrum of Fe^{3+} ions is always observed; for these ions a much smaller initial splitting is characteristic than for Fe^{3+} ions isomorphously replacing Si^{4+} in crystals of natural and synthetic amethysts ($^{4-6}$). Lehmann and Moore suggested (^{7}) that the observed e.p.r. spectrum is due to interstitial Fe^{3+} ions. Indeed, in the structure of α-quartz there is one position lying on the c axis between silicon-oxygen tetrahedra, and a second position lying on the a axis, also between two silicon-oxygen tetrahedra, and in these positions the Fe^{3+} ions are located in distorted tetrahedra of oxygen ions with the following distances to the nearest oxygens: $R_{1,2} = 2.544$, $R_{3,4} = 2.65$ for the first position, and $R_{1,2} = 2.644$, $R_{3,4} = 2.70$ for the second position (^{7}). In both cases, three equivalent paramagnetic centers should be observed in

Fig. 1

Figure 1: Fig. 1

Fig. 2

Figure 2: Fig. 2

the unit cell. When the crystal is oriented so that its *c* axis is parallel to the direction of the magnetic field, these three positions become indistinguishable. Indeed, the e.p.r. spectrum of Fe^{3+} in brown quartz is characterized by three equivalent positions of the Fe^{3+} ion in the unit cell, with the three lines of each transition merging into one at $H \parallel c$. Judging from the small value of the ratio E/D, it may be assumed that the observed e.p.r. spectrum in brown quartz is associated mainly with Fe^{3+} ions in the second position, i.e., in the relatively less distorted tetrahedron.

In brown quartz the intensity of the EPR lines of Fe^{3+}, upon slow heating to 400–450° and careful cooling, decreases only slightly, while the brown color of the specimens changes to greenish. High-temperature annealing (at 600–700°) leads to clouding of brown and green crystals, with the brown zones (in zonal polychromy) usually becoming less cloudy than the green ones. It has also been established that the intensity of clouding is proportional to the intensity of the coloration. As D. D. Melankholin and I. P. Guseva showed ([8]), primarily green crystals exhibit considerably greater light scattering than brown ones. According to EPR data, during high-temperature annealing the interstitial Fe^{3+} centers are practically completely destroyed. In green (irradiated) crystals an EPR spectrum of Fe^{3+} is observed that is analogous to that observed in the brown layers of the same crystals, but of somewhat lower intensity.

For the optical absorption spectra of quartz with brown coloration, strong absorption in the violet and ultraviolet regions is characteristic (Fig. 1). The brown coloration is dichroic, especially in the short-wavelength region, with $D_o > D_e$. Green coloration differs from brown by increased absorption in the region 7000–11 000 Å, where absorption bands at 7400 and 9600 Å are clearly revealed, with an almost complete absence of dichroism (Fig. 1).

Fig. 1. Optical absorption spectra of synthetic quartz with brown (2—initial coloration, 1—after annealing at $\sim 500°$) and green (3) colorations. The symbols *e* and *o* indicate the absorption curves for the ordinary and extraordinary waves, respectively

Fig. 2. Optical absorption spectrum of synthetic quartz with blue coloration

In crystals of blue quartz no EPR spectrum associated with Co^{2+} is observed (measurements were carried out on an 8-mm radio spectrometer at liquid-helium temperature). The optical absorption of blue quartz is characterized by a broad band with three maxima at 5400, 5950, and 6400 Å, with a complete absence

Figure 3

Figure 3: Figure 3

of dichroism (Fig. 2).

Earlier electron-microscopic studies showed (9) that colorless synthetic quartz crystals that become cloudy upon annealing contain (in contrast to non-clouding ones) particles of a nonstructural impurity with diameter $\sim$ 0.2-0.3 μ. When crystals are annealed to a temperature of 500°, coarsening of impurity particles occurs and a network of microcracks forms near them, with which, evidently, the process of clouding of such crystals is mainly connected. Study of brown quartz crystals showed,

Fig. 3. Electron-microscopic images of mica surfaces: **a** –pure quartz after etching in a 10% HF solution for 30 s; **b** –brown quartz after etching in a 10% HF solution for 30 s; **c** –green quartz; **d** –blue quartz; **e** –brown quartz after annealing at $T \sim 500^\circ$; **f** –brown quartz after annealing at $T \sim 700^\circ$. All images were made using platinum-carbon replicas.

that they do not contain sufficiently large and isolated inclusions (i.e., inclusions sufficiently large and isolated to be detected by the electron-microscopic method), although the structure of such crystals is looser than that of non-turbid quartz crystals (as is revealed by prolonged etching (Fig. 3a, b)). At the same time, spheroidal inclusions are found in green and blue quartz crystals, close in size to those observed in quartz crystals with an unstructured impurity (Fig. 3c, d). As already noted, upon annealing an irreversible transition of the brown coloration to green takes place. Simultaneously, the colloidally dispersed inclusions coarsen, up to sizes of 600-800 Å, and their number naturally decreases (Fig. 3e, f). It is also possible that, during annealing, in addition to aggregation of colloidal particles, chemical changes in the iron silicates occur and iron passes from the trivalent form predominantly into the divalent form, which is manifested in absorption bands at 7400 and 9000 Å, characteristic of silicate glasses containing an admixture of divalent iron (12). During annealing, a large fraction of the interstitial Fe^{3+} ions enters, as a result of diffusion and destruction of individual regions of the quartz structure, into the colloidally dispersed inclusions (disappearance of the characteristic EPR spectrum).

The data presented indicate that the blue and green colorations of quartz are associated with colloidally dispersed inclusions of cobalt and iron silicates, respectively, and that the absorption bands observed in blue quartz may be assigned to transitions between the $^4A_2 \rightarrow {}^4T_1(F)$ states (10), characteristic of tetrahedral cobalt complexes. The Co^{2+} ions are evidently located in the silicate inclusions (which explains the absence of the EPR spectrum of Co^{2+} in these crystals), and do not isomorphously replace Si^{4+} in the quartz structure, as A. Ballman suggested (11).

The brown coloration is most likely caused by a finely dispersed phase of iron silicates, as well as by interstitial Fe^{3+} ions. The dichroism of brown quartz in the short-wavelength part of the spectrum is associated precisely with these Fe^{3+} ions, and the overall high level of optical absorption in brown quartz, as compared with colorless quartz, with a foreign phase of iron silicates. Comparison of the EPR spectra and optical spectra of synthetic brown crystals and natural citrines obtained by careful annealing of certain amethyst samples ([7]) indicates the similarity of the nature of the coloration in these two varieties of quartz.

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