The natural beryl crystals have been irradiated by 40 keV iron ions with fluence of $1.5 \times 10^{17}$ ion/cm$^2$ on an ion beam accelerator. For an annealing of radiation defects and a redistribution of implanted iron ions, the thermal treatment of irradiated beryls has been performed in oxygen during 30 min. at 600 °C. Crystal-chemical peculiarities of irradiated beryls were then investigated by optical absorption and Mössbauer spectroscopy. Iron irradiation and following a thermal annealing of non-colored beryl have led to alteration of color of crystals into orange-yellow. It was established that the iron ions implanted in beryl's structure are localized in octahedral and tetrahedral sites, where they substitute aluminum and beryllium ions by isomorphous way.

I. INTRODUCTION

Beryl is a representative of ring-type silicate crystal whose crystalline structure was firstly described by W.L. Bragg in 1926 [1]. The beryl structure of hexagonal form is built from the rings composed from six silicon-oxygen tetrahedrons. The silicon-oxygen rings form the empty channels oriented along a crystalline axis $c$ and which are connected in a common crystal lattice by Al$^{3+}$ cations in a surrounding of six oxygen ions and by Be$^{2+}$ cations in a quarter oxygen surrounding (fig. 1).

It is well known that a single crystal of pure beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ is colorless and transparent. However, if beryls contain small amount of some transition metal as an impurity in crystalline sites, they may show various color tones. For example [2], the green color of emerald is ascribed to a small amount of Cr$^{3+}$ ions localized in aluminum positions, and the pink beryl (morganite) is colored by Mn$^{2+}$ ions localized in aluminum positions, and the pink beryl (morganite) is colored by Mn$^{2+}$ ions. It is well known that a single crystal of pure beryl $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ is colorless and transparent. However, if beryls contain small amount of some transition metal as an impurity in crystalline sites, they may show various color tones. For example [2], the green color of emerald is ascribed to a small amount of Cr$^{3+}$ ions localized in aluminum positions, and the pink beryl (morganite) is colored by Mn$^{2+}$ ions.

Different relations of the amount of the Fe$^{2+}$ and Fe$^{3+}$ impurity in structural positions of Be$^{2+}$, Al$^{3+}$ or Si$^{4+}$ determine the color of the Fe-containing beryls from blue aquamarines to yellow-orange heliodors. As rule, the color of beryl is not changing if the metal impurity is in interstitial positions and structure channels of the crystal.
Ion beam implantation can introduce any chemical element in the near-surface layer of materials, and it may be a tool for a synthesis of new materials and ion modification of physical properties of the irradiated substrate. This technique was rapidly found the practical applications in many fields, e.g. semiconductors, metals and so on [3]. As yet, however, very little work has been published on the coloring of dielectric crystals by implantation of transition metal ions [4-6]. Especially it is noted to natural minerals. To our knowledge there is only paper [7] on the coloring of natural topazes in pale green tone by implantation of chromium ions. In this report we present experimental results on the coloring of natural colorless beryl by iron implantation. Although as-implanted sample showed only dark grey tone, the color of the implanted beryl had
been changed to orange-yellow with golden luster after thermal annealing. The optical and Mössbauer spectra of the annealed beryl are presented to determinate the color nature, valence state and lattice positions of implanted iron ions.

II. EXPERIMENTAL

The colorless and transparent crystal of Ural natural beryl (goshenite) was the subject of our experiments. At first stage the crystal cut and polished into shape of the flat plates with the thickness is equal 2 mm. The direction of a normal to plate plane was parallel to crystallographic axis c (fig.1). Then the beryl plates were used as a substrates for ion beam irradiation. The 40 keV Fe+ ions were implanted into the beryl substrates with the fluence (dose) of $1.5 \times 10^{17}$ ion/cm$^2$ and at constant ion current density 10 μA/cm$^2$ on an ion beam accelerator ILU-3. Thermal annealing of implanted beryl substrates was performed in an electric furnace in an oxygen atmosphere at temperatures in the range 400-800 °C for 30 min. The orange-yellow sample of beryl under study was obtained after annealing at temperature is equal 600 °C. Optical absorption spectra of natural and colored beryl were measured in the range from 400 to 1000 nm by using the special microprobe optical setting. Mössbauer absorption spectra were recorded at room and liquid nitrogen temperatures on standard spectrometer equipped with Cr matrix $^{57}$Co source of γ-ray. Speed scale was calibrated relative to pure bulk iron.

III. RESULTS AND DISCUSSION

The iron irradiation leads to the decrease of beryl transparency and to the alteration of crystal color into dark grey. This fact is known for transparent silicate crystals being under irradiation [8], and that is connected with radiation damage of beryl crystalline structure during metal implantation. At high dose of irradiation, the near-surface layers of silicate crystals are in an amorphous state that leads to a loss of transparency and to dark grey color of crystal. The thermal treatment of irradiated crystals is usually required to anneal the radiation defects. It was established that the transparency and color of implanted beryl samples are changed during thermal treatment, depending on temperature (T) of annealing. Namely, the transparency of sample annealed at T=400 °C became higher than that in as-implanted beryl. The color of such sample is a pale grey after annealing. The increase of sample transparency suggests that the damage region of irradiated crystal was partly reconstructed after thermal treatment. The transparency was further increased for another sample annealed at T=600 °C. The color tone turned to yellow-grey after first 10 minutes of annealing. The yellowish tone was enhanced and the color of irradiated beryls became orange-yellow with golden luster after 30 minutes of annealing. In mineralogy, the natural beryls with such color tone are known as “goldberyls” [2]. The surface cracks and internal crystal splits take place in the orange-yellow beryls obtained after annealing at higher temperature is equal 800 °C.

Figure 2 shows the optical absorption spectra of both natural colorless beryl (spectrum A) and the synthesized goldberyl (spectrum B) obtained after annealing at T=600 °C for 30 min. As is seen, there are two wide bands of absorption in the infrared and visible ranges of optical spectra,
respectively. The first band is observed in the infrared range at wavelength is equal 820 nm for both presented spectra. This infrared absorption is generally ascribed to internal electron transition of Fe$_{VI}^{2+}$ ions localized in octahedral aluminum sites of natural crystal, and ones does not affect on the coloring of beryls [2,9].

![Optical absorption spectra of natural colorless beryl (A) and yellow-orange beryl (B) synthesized by iron implantation with following a thermal annealing](image)

**Fig. 2.** Optical absorption spectra of natural colorless beryl (A) and yellow-orange beryl (B) synthesized by iron implantation with following a thermal annealing

The absorption in the visible range only determines the color of different natural minerals. As can see from Fig.1, the absorption in visible range (second wide band in our spectra) is more intensive in the synthesized goldberyl than that in natural crystal. Especially it is pronounced in the violet part of optical spectrum, and that determines the orange-yellow coloring of synthesized goldberyl. According to [2,9], the absorption bands of Fe-containing beryls in visible range are connected with charge (electron) transfers ligand $\rightarrow$ metal in different FeO-polyhedrons and with intervalence charge transfers in exchange-coupled pairs of Fe$_{IV}^{2+} \rightarrow$ Fe$_{VI}^{3+}$ and Fe$_{VI}^{2+} \rightarrow$ Fe$_{VI}^{3+}$. It is accepted that the yellow color of heliodors is mainly determined by charge transfers O$^{2-} \rightarrow$ Fe$_{VI}^{3+}$ and O$^{2-} \rightarrow$ Fe$_{IV}^{2+}$, Fe$_{IV}^{3+}$ [9]. Thus, the analysis of optical spectrum
of synthesized goldberyl point out that the iron ions implanted in beryl are localized in octahedral and tetrahedral sites.

This supposition was confirmed by Mössbauer study of the synthesized goldberyl. Figure 3 shows the Mössbauer spectra of the natural (A) and the synthesized goldberyl (B), respectively. As is seen, the shapes of the spectra are different in low and middle velocity ranges. Experimental spectra were analyzed in the assumption of three overlapping doublet components by using standard mathematical procedure. These three components of Mössbauer spectra are presented on Fig 3 by thin lines with indexes 1, 2 and 3, respectively. The hyperfine parameters of each component: isomer shift (IS), quadrupole splitting (QS) and relative area of component (R) are listed in Table 1 for room and liquid nitrogen temperatures. The calculated values of hyperfine parameters were compared with the results of other Mössbauer studies of Fe-containing beryls [9,10]. The comparative analysis indicates that the first spectrum component (first doublet) matches to FeV₁²⁺ ions localized in Al³⁺ crystalline sites in both natural crystal and synthesized goldberyl. According to above analysis of optical spectra these FeAl²⁺ ions do not affect the color of beryl crystals. Note that the intensity (area) of this spectrum component (not presented in Table 1) is near equal in both the natural and the synthesized goldberyl. In other words the iron occupancy of this structural positions has not changed after implantation of beryl.

Fig. 3 Room temperature Mössbauer spectra of natural colorless beryl (A) and yellow-orange beryl (B) synthesized by iron implantation with following a thermal annealing.
Table 1. Hyperfine parameters of three Mössbauer components presented on Fig. 3

<table>
<thead>
<tr>
<th></th>
<th>Natural beryl</th>
<th>Synthesized goldberyl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T=295</td>
<td>T=100 K</td>
</tr>
<tr>
<td><strong>1st- doublet</strong></td>
<td>FeAl^{3+}</td>
<td>FeAl^{3+}</td>
</tr>
<tr>
<td>IS (mm/sec.)</td>
<td>1.25</td>
<td>1.35</td>
</tr>
<tr>
<td>QS (mm/sec.)</td>
<td>2.49</td>
<td>2.53</td>
</tr>
<tr>
<td>R (%)</td>
<td>68.58</td>
<td>36.69</td>
</tr>
<tr>
<td><strong>2nd - doublet</strong></td>
<td>Fe^{2+}</td>
<td>FeBe^{2+}</td>
</tr>
<tr>
<td>IS (mm/sec.)</td>
<td>0.98</td>
<td>1.09</td>
</tr>
<tr>
<td>QS (mm/sec.)</td>
<td>1.60</td>
<td>1.25</td>
</tr>
<tr>
<td>R (%)</td>
<td>14.77</td>
<td>11.29</td>
</tr>
<tr>
<td><strong>3rd - doublet</strong></td>
<td>Fe^{3+} in interstitial positions</td>
<td>FeAl^{3+} or FeBe^{3+}</td>
</tr>
<tr>
<td>IS (mm/sec.)</td>
<td>0.13</td>
<td>0.25</td>
</tr>
<tr>
<td>QS (mm/sec.)</td>
<td>0.58</td>
<td>0.46</td>
</tr>
<tr>
<td>R (%)</td>
<td>16.65</td>
<td>52.19</td>
</tr>
</tbody>
</table>

As seen from Table 1, the main difference is observed for second and third spectrum components whose relative areas (R) are larger in Mössbauer spectrum of the synthesized goldberyl than that in natural beryl. The hyperfine parameters of these components correspond to double-charged iron ions in square-coordinate positions (second doublet) and triple-charged iron ions in beryl crystals (third doublet) [9,10]. Thus, the most of iron ions implanted in beryl seems to be found in Fe^{2+} and Fe^{3+} valence states, that is in agreement with our analysis of optical spectrum of the synthesized goldberyl. Weak temperature dependence of relative area of second doublet and high values of IS and QS indicate that Fe^{IV}^{2+} ions are in Be-sites in both natural crystal and synthesized goldberyl.

The strong temperature dependence of relative area of third doublet for natural crystal indicates that the Fe^{3+} ions corresponding to this doublet are located in the interstitial positions and structure channels. Contrary to that the weak dependence of quantity R for third component on temperature was observed in the synthesized goldberyl. This fact points out that the Fe^{3+} ions are strongly bounded to the lattice and localized in the crystal sites of goldberyl. The high QS value of Fe^{3+} ions indicates that the iron ions are occupied either the tetrahedral or distorted octahedral sites of crystal where they substitute beryllium and aluminum ions, respectively.
CONCLUSION

The natural colorless beryl have been irradiated by 40 keV Fe⁺ ions with high fluence. It was established that iron irradiation with following a thermal annealing of beryl lead to yellow-orange coloring of crystal. Crystal-chemical peculiarities of colored beryl were investigated by optical absorption and Mossbauer spectroscopy. Analysis of the experimental results shows that the most of implanted iron ions are in both Fe²⁺ and Fe³⁺ electrical states where they substitute beryllium and aluminum host ions in regular sites, respectively. The presented results may be useful for gemology from a point of view of production of novel colored gemstones by implantation of transition metals in natural crystals.

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REFERENCES


