
NOTES · AND · NEW TECHNIQUES

HYDROTHERMALLY GROWN SYNTHETIC AQUAMARINE MANUFACTURED IN NOVOSIBIRSK, USSR

By Karl Schmetzer

Physical, chemical, spectroscopic, and microscopic characteristics of a sample of hydrothermally grown synthetic aquamarine from the USSR are presented. Physical and spectroscopic data are correlated with the chemical composition of the synthetic beryl to establish cause of color. Diagnostic criteria to separate natural from synthetic aquamarine are given, and the growth conditions of this synthetic blue beryl are discussed. This is the first description of synthetic aquamarine in the English gemological literature.

In the course of experimental investigations of Russian hydrothermally grown synthetic emeralds (e.g., Schmetzer, 1988), the author consulted with Dr. A. S. Lebedev, of the Institute of Geology and Geophysics, Siberian Branch of the USSR Academy of Sciences, Novosibirsk. Dr. Lebedev, who helped develop the hydrothermal synthesis of emeralds, gave the author several specimens of hydrothermally grown synthetic beryl doped with different transition metal oxides. For those synthetic beryl samples doped with cobalt, nickel, or copper, no natural counterparts are known. This is not the case, however, for the iron-bearing blue synthetic beryl that resembles the gem variety aquamarine.

Although iron-doped synthetic aquamarines have been described in the Russian literature (e.g., Klyakhin et al., 1981; Pugachev, 1984), the specimen received from Dr. Lebedev is the first synthetic aquamarine the author has seen. At present, there is no commercial production of synthetic

aquamarine in the USSR, although such production is planned for several new gem materials (Dr. A. Rodionov, Novosibirsk, pers. comm., 1989). Since there is no technical obstacle to a commercial synthesis of aquamarine in the USSR, it is possible that this will be one of the materials released. Accordingly, this article provides what the author believes to be the first description of synthetic aquamarine available in the English gemological literature.

MATERIALS AND METHODS

The rough specimen of synthetic light blue beryl examined (figure 1) was a slice of a crystal that measured about 1 cm in diameter. One 0.29-ct rectangular faceted sample (figure 2) was cut from the crystal slice.

Refractive indices were obtained by a standard gemological refractometer, and specific gravity was determined hydrostatically. Unit-cell parameters were determined by X-ray powder diffraction using a Guinier camera and refined from 27 measured d-values. Microprobe analysis was per-

ABOUT THE AUTHOR

Dr. Schmetzer is a research scientist residing in Petershausen, near Munich, Germany.

Acknowledgments: The author is grateful to Dr. A. S. Lebedev of the USSR Academy of Sciences, Novosibirsk, who kindly supplied the specimen of synthetic aquamarine examined for this article.

All photomicrographs are by the author.

Gems & Gemology, Vol. 26, No. 3, pp. 206-211

© 1990 Gemological Institute of America

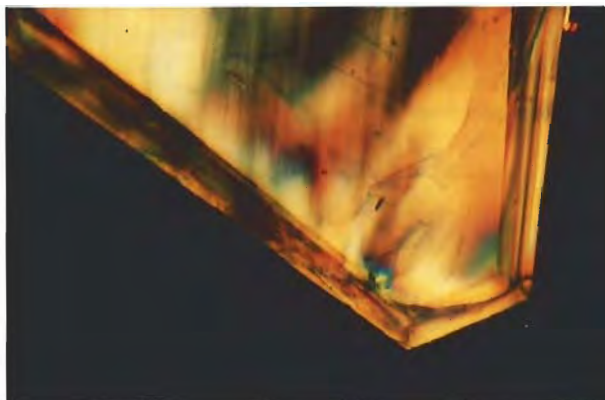


Figure 1. The rough synthetic aquamarine crystal from which this 1-cm-diameter slice was cut was hydrothermally grown at the Institute of Geology and Geophysics, Novosibirsk, USSR. A view parallel to the *c*-axis reveals the presence of three distorted prism faces $m(10\bar{1}0)$. Crossed polarizers, magnified $30\times$.

formed on an ARL SEMQ instrument with an operating voltage of 20 kV and a beam current of 10 nA; values were calculated by the MAGIC IV correction program provided by the manufacturer. Spectral data in the U.V.–visible range were obtained with a Leitz-Unicam Model SP.800 spectrophotometer, and infrared spectra were obtained with a Perkin Elmer Model IR 180 infrared spectrometer. Photomicrography was performed on a Schneider immersion microscope with Zeiss optics.

VISUAL APPEARANCE

The sample revealed three highly distorted prism faces $m(10\bar{1}0)$, as well as one nearly planar surface that had been sawn parallel to the boundary of the synthetic aquamarine with the colorless beryl seed. This boundary is at a 32° angle with the *c*-axis of the synthetic beryl crystal. The light blue faceted piece has a pleochroism of medium intense blue parallel to the *c*-axis and light yellowish green perpendicular to the *c*-axis.

PHYSICAL, CHEMICAL, AND SPECTROSCOPIC PROPERTIES

Optical and Physical Properties. The specific gravity (measured as 2.69 and calculated as 2.694) and refractive indices ($n_o = 1.583$, $n_e = 1.575$, birefringence = 0.008) of the sample of synthetic light blue beryl examined are within the range known for natural aquamarines. The unit-cell dimensions of this particular synthetic aquamarine ($a_0 = 9.224 \text{ \AA}$, $c_0 = 9.200 \text{ \AA}$, $c/a = 0.9974 \text{ \AA}$) are identical,



Figure 2. A 0.29-ct stone ($4.61 \times 4.57 \times 2.06 \text{ mm}$) was faceted from the synthetic aquamarine slice shown in figure 1. Photo by O. Medenbach, Bochum, Germany.

within the limits of experimental error, to those reported by Pugachev (1984).

Chemical Analysis. A chemical analysis of the specimen was provided by the producer (table 1). These data are identical to those reported for the synthetic aquamarine described by Pugachev (1984) as sample No. 131 and suggested that the sample received from Novosibirsk was part of Pugachev's specimen No. 131; this was subsequently confirmed (A. S. Lebedev, pers. comm., 1989).

Microprobe analyses performed for this study confirmed the chemical properties submitted by the producer and reported by Pugachev (table 1), with one small but remarkable difference: The distinct amounts of nickel detected in this sample were not mentioned by Pugachev (1984).

It is worth noting here that the high Fe content of these synthetics is accompanied by low Mg and Na. By comparison, while these same elements can vary considerably in natural aquamarines, it is the author's experience that high Fe contents usually correlate with high Na and Mg in the natural stones.

Spectroscopy. Absorption spectra in both the visible and ultraviolet ranges revealed the presence of distinct absorption bands of iron and nickel (table 2, figure 3; cf. Schmetzer, 1988), which is consis-

TABLE 1. Chemical composition of a hydrothermally grown synthetic aquamarine from the USSR (in wt.%).

Oxide	This study (range of 5 microprobe analyses) ^a	As provided by manufacturer and published in Pugachev (1984)
Li ₂ O	NA	0.20
BeO	NA	13.24
Na ₂ O	<0.02	ND
Al ₂ O ₃	16.90–17.35	16.96
SiO ₂	64.42–65.35	64.76
Fe ₂ O ₃ ^b	2.67– 2.99	2.82
Ni ₂ O ₃ ^b	0.01– 0.02	ND
CuO	<0.01	ND
H ₂ O	NA	1.15

^aMgO, K₂O, CaO, and Cs₂O were found to be below detection limits (<0.02 wt%), as were MnO, V₂O₅, and Cr₂O₃ (<0.01 wt%). NA = not analyzed; ND = not determined.

^bTotal iron as Fe₂O₃ and total nickel as Ni₂O₃.

tent with the chemical data (table 1). Infrared spectroscopy confirmed the presence of water molecules and lithium ions in channel sites of the beryl structure (figure 4) and, therefore, the hydrothermal origin of the sample (cf. Schmetzer, 1989). The infrared spectra revealed three absorption maxima, at 3694 cm⁻¹ (designated band A, assigned to non-alkali-bonded water molecules) and at 3592 cm⁻¹ and 3655 cm⁻¹ (designated bands B and C, both assigned to alkali-bonded water molecules). The presence of lithium in channel sites is

Figure 3. The U.V.-visible absorption spectrum of the sample of synthetic aquamarine reveals typical aquamarine absorption bands, caused by ferric and ferrous iron, on which a weak nickel spectrum is superimposed (not visible at scale illustrated).

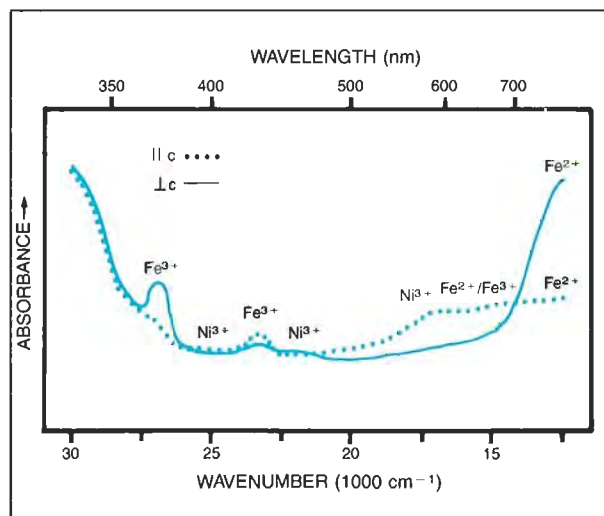


TABLE 2. Spectroscopic features of a hydrothermally grown synthetic aquamarine from the USSR.

Absorption maxima		Polarization ^a	Assignment ^b
nm	cm ⁻¹		
833	12,000	c	Fe ²⁺ /oct.
820	12,200	⊥ c	Fe ²⁺ /tet.
752–599	13,300–16,700	c	Fe ^{2+/3+} /oct.
606	16,500	c	Ni ³⁺ /oct.
595	16,800	c	Ni ³⁺ /oct.
455	22,000	⊥ c	Ni ³⁺ /oct.
426	23,500	c > ⊥ c	Fe ³⁺ /oct.
413	24,200	⊥ c	Ni ³⁺ /oct.
370	27,000	⊥ c >> c	Fe ³⁺ /oct.

^a|| c = parallel to c-axis, and ⊥ c = perpendicular to c-axis.

^bSee Schmetzer 1988.

confirmed by the absence of distinct amounts of sodium (again, see table 1). In general, these spectra are typical of those that have been measured for natural aquamarines from various localities.

Figure 4. The infrared absorption spectrum of the sample of synthetic aquamarine reveals absorption bands of non-alkali-bonded (A) and alkali-bonded (B and C) water molecules, which prove the hydrothermal origin of the sample.

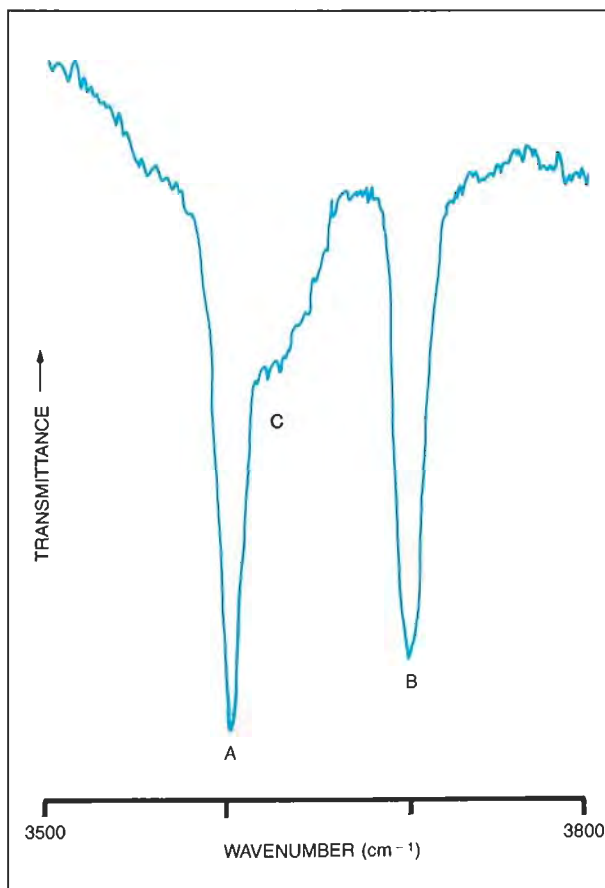




Figure 5. In the faceted sample of Russian hydrothermally grown synthetic aquamarine, "feathers" consisting of either liquid or two-phase inclusions are found in both the seed (above) as well as in the light blue portion (below). Immersion, magnified 40 \times .

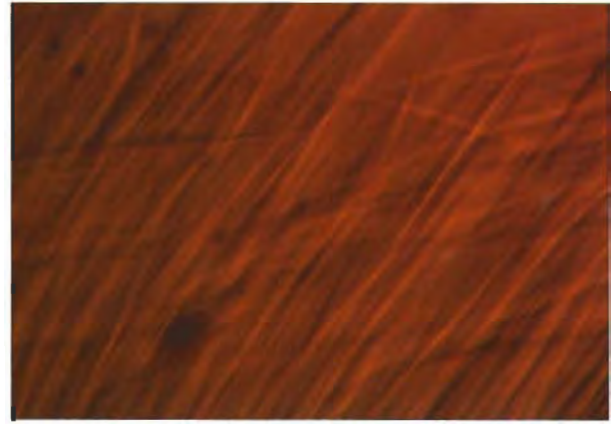


Figure 6. Irregularly changing subgrain boundaries between subindividuals in Russian hydrothermally grown synthetic aquamarine are among the diagnostic characteristics of this material that can be used to distinguish it from natural aquamarine. Immersion, magnified 60 \times .

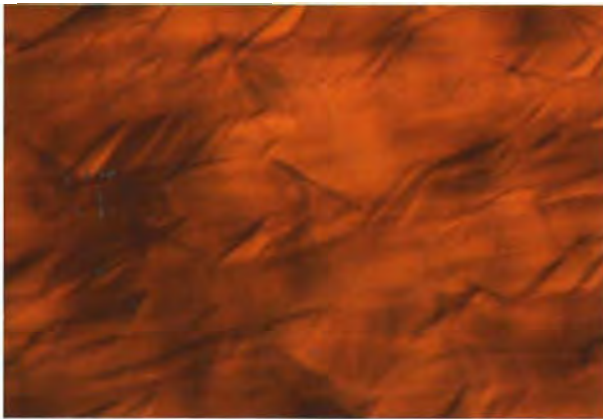


Figure 7. The cellular pattern of the subgrain boundaries described in figure 6 is similar to that described for synthetic emeralds that have been hydrothermally grown in the USSR. Immersion, magnified 60 \times .

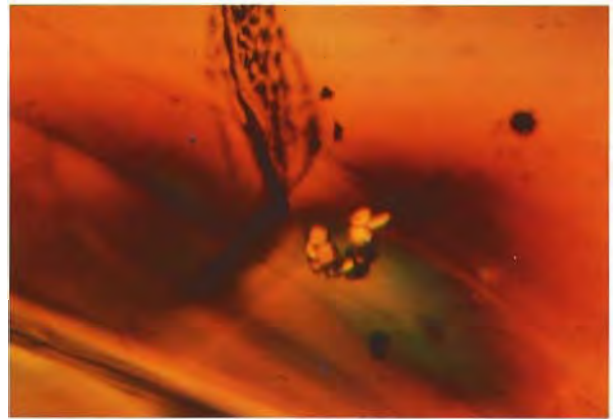


Figure 8. The sample hydrothermally grown synthetic aquamarine was also observed to contain groups of doubly refractive transparent inclusions as well as opaque hexagonal platelets. Immersion, crossed polarizers, magnified 100 \times .

MICROSCOPIC CHARACTERISTICS

Microscopic examination revealed a distinct boundary between the almost-colorless seed and the synthetic light blue beryl. The similarity in growth features and inclusions between the seed and the synthetic aquamarine grown from it suggested that the seed is also a synthetic hydrothermally grown beryl (figure 5). The fact that the seed/synthetic aquamarine boundary formed an angle of about 32° with the c-axis of the synthetic beryl indicates that the seed plate used had been sawn parallel to the face (5 5 $\bar{1}0$ 6). The same seed-plate orientation was observed for hydrothermal synthetic emerald grown in the USSR (Schmetzer, 1988).

In the immersion microscope, extremely weak growth zoning was observed in the synthetic aquamarine parallel to the boundary with the seed plate. Although this zoning is much weaker than the distinct growth and color zoning noted in synthetic Russian emerald from the USSR, in oblique orientation to this plane there can be observed subgrain boundaries between subindividuals (figure 6), as well as a typical cellular structure (figure 7) that has also been described for the hydrothermally grown synthetic emerald.

The synthetic aquamarine examined contained several groups of small, doubly refractive crystals as well as several hexagonal opaque platelets, possibly hematite (figure 8; cf. Schmetzer,

1988, and Klyakhin et al., 1981). Irregularly shaped cavities with multiphase fillings were also observed, as were two different types of "feathers": nearly planar "feathers" with liquid and two-phase fillings, and residues of the growth solution trapped in the form of twisted veil-like "feathers" (again, see figure 5).

DISCUSSION

Crystal Chemistry and Color. The iron absorption bands observed in the visible and ultraviolet spectra of this synthetic sample are typical of those seen in natural aquamarine. Three different types of iron are responsible for the blue coloration of aquamarine (for further details as well as for a summary of the literature, see Schmetzer, 1988). According to Solntsev et al. (1984, 1985), the synthetic-aquamarine spectrum described here reveals absorption bands of divalent and trivalent iron in octahedral aluminum sites as well as bands of divalent iron in tetrahedral beryllium sites (table 2). The blue color of the sample is due to a strong and broad absorption in the red and yellow areas, which is assigned to a charge-transfer transition between ferric and ferrous iron replacing aluminum in adjacent octahedral sites of the beryl structure.

In the synthetic specimen examined here, weak absorption bands of trivalent nickel (table 2, figure 3) were found superimposed on the normal aquamarine absorption spectrum. Because the nickel doublet in the spectrum parallel to the *c*-axis at 606 and 595 nm—i.e., in the yellow to orange range—is superimposed on the dominant color-causing $\text{Fe}^{2+}/\text{Fe}^{3+}$ charge-transfer band, it intensifies the blue coloration. On the other hand, the nickel absorption band in the spectrum perpendicular to the *c*-axis at 455 nm—i.e., in the blue to bluish green range—is responsible for an absorption minimum in the green. Thus, the light blue coloration of nickel-free natural aquamarine is converted to a light yellowish green in the nickel-bearing synthetic specimen examined.

The presence of water and lithium in combination with the absence of sodium (table 1) indicated assignment of the absorption bands in the infrared between 3500 cm^{-1} and 3800 cm^{-1} to non-alkali-bonded and lithium-bonded water molecules in channel sites of the beryl lattice (Schmetzer, 1989). However, it is also generally accepted that part of the lithium replaces beryllium in tetrahedral sites. These basic crystal chemical considerations are confirmed by the unit-cell dimensions of the

synthetic aquamarine, the *c/a* value of which is typical for "normal" beryl, in which both octahedral and tetrahedral substitutions occur to a limited extent (Aurisicchio et al., 1988).

GROWTH CONDITIONS OF SYNTHETIC AQUAMARINES

According to the Russian literature (Klyakhin et al., 1981; Pugachev, 1984; Solntsev et al., 1984, 1985), the synthetic aquamarine is grown in stainless steel autoclaves without noble metal inserts. The following growth conditions were published: temperature, 590° – 610°C ; temperature gradient, 70° – 130°C ; and pressure, 1000–1500 bars. Since nutrient oxides of beryllium, aluminum, and silicon are used, the high iron content (and the small amount of nickel, as has been confirmed by A. S. Lebedev, pers. comm., 1989) must derive from the walls of the steel autoclaves. As mentioned above, the seed used is probably a synthetic colorless beryl. The synthetic crystals grow at a rate of 0.32 mm per day.

To grow blue aquamarine rather than iron-bearing colorless beryl, the process must incorporate large amounts of divalent iron (Fe^{2+}) into octahedral sites of the lattice. This is accomplished by adding to the solution variable quantities of iron-carbonyl (to reduce oxygen partial pressures) and lithium salts (to provide the charge-compensating ion). According to the Russian literature cited, colorless iron-bearing beryl is grown at oxygen partial pressures above the hematite/magnetite equilibrium, and aquamarine is obtained in the wide field of magnetite stability below the hematite/magnetite line. The most intense coloration was obtained for beryl samples grown under oxygen partial pressures in the magnetite stability field close to the magnetite/iron equilibrium.

The aquamarine sample examined in the present paper reveals a light blue coloration. The identical specimen reported by Pugachev (1984) was grown at about 600°C under an oxygen partial pressure of $\lg P_{\text{O}_2} = -25$ (Pugachev, 1984; figure 9).

The conditions used by Russian scientists to grow hydrothermal synthetic aquamarine are similar to those they have used to grow hydrothermal synthetic emerald (Schmetzer, 1988). It is likely that identical or almost identical steel autoclaves without precious metal inserts are used, as are similar pressures, temperatures, and temperature gradients. The same orientation of the seed plates is chosen for both. The most important differences are the absence of divalent iron in synthetic

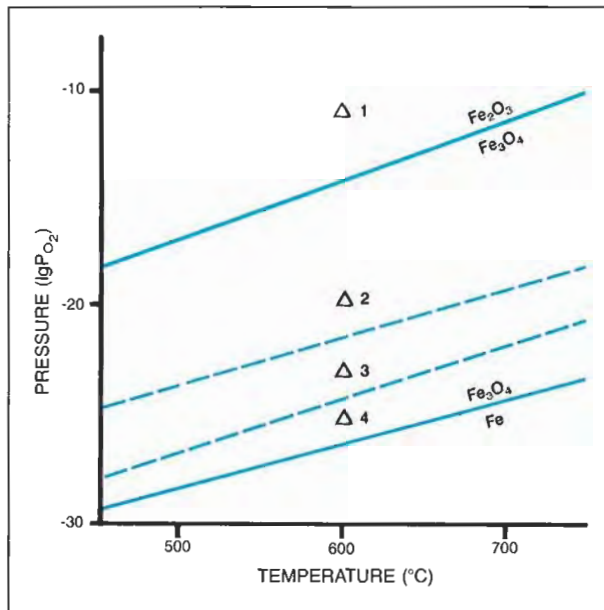


Figure 9. Synthetic iron-bearing beryl was grown at the four positions marked on this pressure-temperature diagram adopted from Pugachev (1984). The samples in group 1, grown under oxygen partial pressures above the hematite/magnetite ($\text{Fe}_2\text{O}_3/\text{Fe}_2\text{O}_4$) equilibrium line, are colorless. The samples in groups 2, 3, and 4, grown at decreasing oxygen partial pressures in the magnetite stability field, reveal increasing intensities of blue color. The specimen examined for this article probably belongs to group 3.

emerald, and the absence of chromium and of high amounts of copper and nickel in synthetic aquamarine. These differences would appear to be the result of the different oxides used as nutrients during growth as well as the different oxygen partial pressures.

DISTINCTION OF NATURAL FROM SYNTHETIC AQUAMARINE

The most characteristic features of this synthetic aquamarine are the growth structures, that is, the subgrain boundaries between cellular subindividuals (figures 6 and 7), which are caused by the orientation of the seed plate parallel to the crystal face (5 5 $\bar{1}0$ 6). Also readily visible with the microscope, when they are present, are residues of the seed plate (figure 5) and small opaque platelets (figure 8). Doubly refractive crystals (figure 8), cavities with multiphase fillings, and various types of planar and twisted feathers (figure 5) may also be conclusive in some cases.

The observation of nickel bands in the visible

range of the absorption spectrum (figure 3) is another clue to the recognition of a blue beryl of unknown origin as synthetic aquamarine. Unfortunately, these features are too weak to be seen with a hand spectroscope. These traces of nickel are caused by the use of stainless steel autoclaves without precious metal inserts. Of course, if a different type of autoclave were to be used in future production, this criterion could be changed. If chemical data can be obtained, the absence of distinct amounts of sodium and magnesium in combination with a high iron content (table 1) also indicate that the material is synthetic aquamarine.

Specific gravity, refractive index, and the infrared spectrum of the hydrothermally grown synthetic aquamarine from the USSR are all within the ranges for natural aquamarines.

SUMMARY AND CONCLUSION

Synthetic aquamarine has been manufactured in the USSR for experimental purposes. No technical obstacles to the commercial growth of synthetic aquamarine are known. The growth technique is similar to that used to manufacture hydrothermal synthetic emeralds in the USSR. The color is the result of a charge-transfer process. The synthetic aquamarine examined showed several microscopic features that would serve to separate it from its natural counterpart.

REFERENCES

- Aurisicchio C., Fioravanti G., Grubessi O., Zanazzi P.F. (1988) Reappraisal of the crystal chemistry of beryl. *American Mineralogist*, Vol. 73, pp. 826-837.
- Klyakhin V.A., Lebedev A.S., Il'in A.G., Solntsev V.P. (1981) Growing of hydrothermal beryl [in Russian]. *Sintez i Vyrashchivanie Optich. Kristallov i Yuvelir. Kamnei*, Novosibirsk 1981, pp. 45-66.
- Pugachev A.I. (1984) Effect of P_{O_2} on structural impurities of iron in hydrothermal beryl [in Russian]. *Fiziko-Khimiya Issled. Sul'fidnykh Silik. Sist.*, Novosibirsk 1984, pp. 87-93.
- Schmetzer K. (1988) Characterization of Russian hydrothermally-grown synthetic emeralds. *Journal of Gemmology*, Vol. 21, No. 3, pp. 145-164.
- Schmetzer K. (1989) Types of water in natural and synthetic emerald. *Neues Jahrbuch für Mineralogie Monatshefte*, No. 1, pp. 15-26.
- Solntsev V.P., Bukin G.V., Klyakhin V.A., Likhova G.G., Pugachev A.I. (1984) Nature of color centers and EPR of iron-containing beryls [in Russian]. *Fiziko-Khimiya Issled. Sul'fidnykh Silik. Sist.*, Novosibirsk 1984, pp. 109-119.
- Solntsev V.P., Bukin G.V., Likhova G.G., Veis N.S. (1985) EPR and optical absorption spectra of iron-containing beryls [in Russian]. *Akademiya Nauk SSSR Sibirskeye Otdeleniye, Trudy Instituta Geologii i Geofiziki. Izdatel'stvo "Nauka" Moscow, USSR*, Vol. 610, pp. 128-134.