

Hole paramagnetic centers in vein granular quartz from the Sakar Mountain in SE Bulgaria

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P. И. Костов — Дырочные парамагнитные центры в жильном гранулированном кварце из горы Сакар в ЮВ Болгарии. Исследование методом электронного парамагнитного резонанса (ЭПР) 17 образцов гранулированного жильного кварца высокой химической чистоты показало, что специфические линии в спектрах ЭПР могут быть использованы для экспрессного определения различных сортов кварца для промышленных нужд, а также для генетических интерпретаций. Набор из трех дырочных центров со специфическими линиями с $g=2.049$, 2.034 и 2.022 принимается за характеристику этого генетического типа кварца. Образцы кварца из гранитоидных вмещающих пород имеют повышенную интенсивность линий ЭПР, интерпретируемых как сумма концентрации дырочных центров в сравнении с образцами из метаморфических вмещающих пород. Контаминированные образцы кварца из контакта обычно имеют повышенную концентрацию дырочных центров в сравнении с образцами из центра жил.

Abstract. Electron paramagnetic resonance (EPR) study of 17 samples of granular vein quartz of a high chemical purity shows, that specific lines in the EPR spectra can be used for an express determination of different quartz grades for industrial purposes, as for genetic interpretations. A set of three hole centers with specific lines at $g=2.049$, 2.034 and 2.022 has been considered as characteristic for this genetic quartz type. Quartz samples from granitoid host rocks have a higher intensity of EPR lines interpreted as a sum of concentration of hole centers compared to those samples from metamorphic host rocks. Contaminated contact quartz samples usually have a higher concentration of hole centers compared to samples from the center of the vein.

Introduction

The Sakar Mountain region has a complex geological setting, its core being built of a granitic pluton elongated in E-W direction with different facies types of granitoids and a contact metamorphic rim including gneisses or gneiss-granites, gneiss-schists and amphibolites (Кожухарова, Кожухаров, 1973; Dabovskii, Naïdutov, 1980).

Granular milky-white quartz veins of nearly monomineral composition are located in the granitoids and also in the metamorphic rocks, forming a few quartz deposits (Асланиян, 1985; Шильфова, Шильфов, 1990), which have been studied as a source of high purity silica raw material of interest for industrial purposes (Боденичаров et al., 1980; Borissov et al., 1982).

Electron paramagnetic resonance (EPR) studies have been carried out in order to study the distribution of the E'_1 centers in granular quartz compared to induced thermoluminescence, showing a low E'_1 concentration and high intensity of thermoluminescence peaks for samples of a granitoid origin, and a high E'_1 concentration but low intensity of thermoluminescence peaks for samples of a metamorphic origin (Костов, 1984; Kostov, 1986). Some other electron-hole centers have been observed in the EPR spectra of quartz samples of the same deposits (Костов, Бершов, 1984).

Infrared spectroscopy studies of water content of this kind of quartz shows relatively low temperatures (Aslanian, Beran, 1986).

In this work a further on study has been provided on the distribution of hole paramagnetic centers in 17 samples from 7 deposits, which are located (Fig. 1) among granitoids (Branitza, Bulgarska Polyana and Hlyabovo) and metamorphic rocks (Bogomil, Mladinovo, Lisovo and Radovetz).

Experiment and results

About 200 mg of powdered quartz vein samples have been studied in the X-band with a ESR 220 spectrometer at room temperature. The method of estimation of the specific lines in the EPR spectra for powdered or polycrystalline quartz has been already discussed (Орленев, 1984; Моисеев, 1985) and in this work for study are used hole centers with g values above 2 with stress on the g_3 values, which have been considered important for distinguishing the nature of the paramagnetic centers (Костов, Бершов, 1987).

In the EPR spectra of granular vein quartz 12 main g values have been listed as characteristic lines (Table 1). Additionally has been measured the intensity of the line at $g=2.01$. The interpretation of the 12 lines is in respect of the g_3 values of possible known paramagnetic centers and that at the 2.01 region can be interpreted as it follows as superpositions of the g_1 and g_2 value line intensities (Костов, Бершов, 1987), so that it shows the sum of concentration of hole centers for a certain sample.

As common for all or most quartz samples are lines in the EPR spectra with $g=2.049$, 2.034 and 2.022, and of course the line at $g=2.01$. The line at $g=2.049$ has been observed in different types rock-forming quartz also. The line at $g=2.034$ previously has

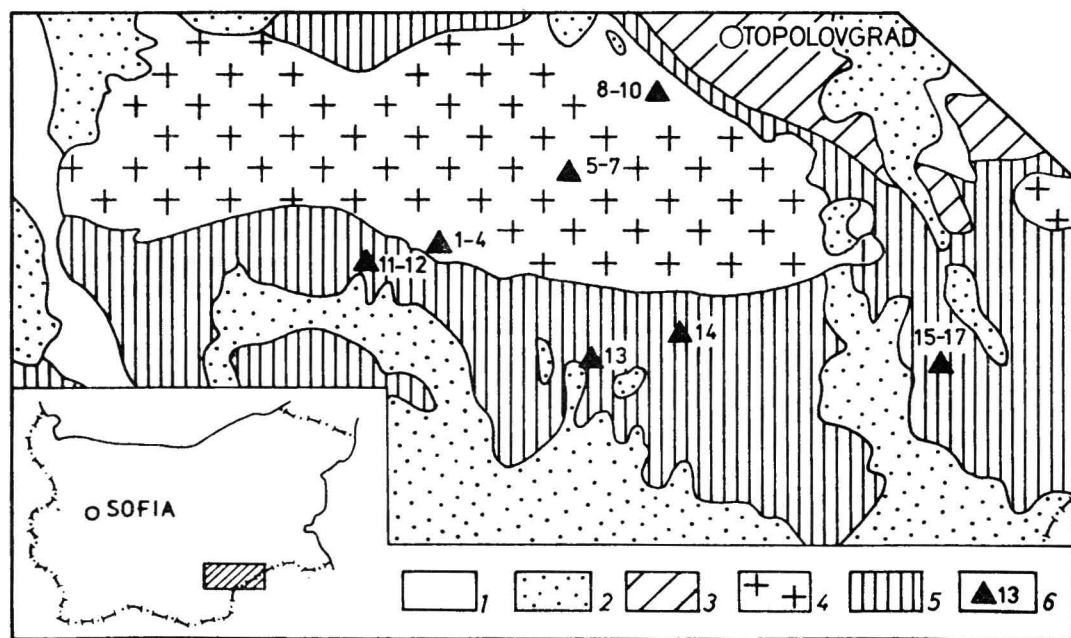


Fig. 1. Geological sketch of the Sakar Mountain region with quartz vein deposits: 1 — Quaternary sediments; 2 — Tertiary sediments; 3 — Triassic metamorphosed sediments; 4 — granitoids; 5 — gneiss-granites, gneiss-shists and other metamorphic rocks; 6 — quartz vein deposits with numbers of samples studied

Table 1

Distribution of paramagnetic hole centers in granular quartz according to specific EPR lines (*g* values): + strong peak; ++ very strong peak. Host rocks: A — granitoids; B — metamorphic rocks

N. Deposit	Colour	2.061	2.052	2.049	2.040	2.038	2.034	2.033	2.032	2.029	2.022	2.020	2.017	2.01 I _{arb} units
A 1 Branitza	white	+	+	+			++			+	+		+	72
2 Branitza	smoky	+	+	+			+	+			++			91
3 Branitza	rose		+	+			+				++			54
4 Branitza	yellow		+	+			++				++			64
5 Bulgarska Polyana	white		+				+				++	+	+	44
6 Bulgarska Polyana	white*		+	+			++				+		+	66
7 Bulgarska Polyana	white		+	+			++				+		+	51
8 Hlyabovo	white	+		+			++				++			33
9 Hlyabovo	white	+		+	+		+	++						69
10 Hlyabovo	white*	+		+			+	+			++			85
B 11 Bogomil	white		+			+	+	++			++			47
12 Bogomil	white*		+	+		+	+				++			48
13 Mladinovo	white			+			++				++			32
14 Lisovo	white	+		+			+			+				50
15 Radovetz	white		+				++				++			34
16 Radovetz	white*			+			+		++		++			51
17 Radovetz	white	+	+	+			+			+	++			57

* Mark for contact samples, which usually are contaminated with other mineral phases.

been reported among chalcedonic and impact quartz, as in morion from pegmatites. The line at $\bar{g}=2.022$ must be declared as characteristic for this specific genetic type of quartz. Peaks' intensity of the lines of the both last centers is high for most of the samples. The line at $\bar{g}=2.01$ has a higher intensity for quartz samples from the granitoids (mean value 63 in arb. units), compared to those from the metamorphic rocks (mean value 46 in arb. units). For coloured quartz samples from a definite deposit the signal intensity of this specific line decreases in the sequence smoky-white-yellow-rose quartz. This signal intensity also is low in white quartz varieties, compared to contaminated contact or coloured samples for a certain deposit. After a 10^{10} Gy dose gamma-irradiation with a Co^{60} source the intensity of this signal increases twice for both genetic types quartz vein samples.

Centers with specific lines at $\bar{g}=2.040$, 2.032 and 2.020 are not discussed as their appearance in the EPR-spectra is in a few cases.

The rest lines with $\bar{g}=2.061$, 2.052, 2.038, 2.033, 2.029 and 2.017 must be attributed to paramagnetic hole centers which are supposed to be typical for a certain deposit, group of deposits or for local geological peculiarities. The first case can be demonstrated by the line at $\bar{g}=2.061$ (N 8-10), 2.038 (N 11-12) or 2.017 (N 5-7).

In addition to the observed signals of paramagnetic hole centers in granular quartz only in two samples (N 6 and 12) the six-component Mn^{2+} structure has been detected.

Discussion

As the models for the different hole centers in quartz are more or less under discussion, suggestion can be made, that the common feature for hole centers must be the substitution of silicon in the SiO_4 tetrahedra by aluminium or another element with some alkalis (Li, Na or K) or hydrogen ions as charge compensators.

The new information on the distribution of hole paramagnetic centers in quartz shows a good agreement with a preliminary study of granular quartz (K o c r o b, B e p-ш o b, 1984). The results on E'_1 center intensities for both genetic types of quartz veins in granitoids and in metamorphic rocks (K o c r o b, 1984) are in a reverse tendency

to the intensities of the signal at $g=2.01$. EPR data for electron and hole centers gives an opportunity for seeking a similar mineral-forming or geological process for the quartz veins at Hlyabovo and Bogomil.

In the case of a high chemical purity of granular quartz the EPR-spectra can be used for justification of electron-hole center concentration for a single quartz vein, group of veins or georegion of distribution of fields of quartz veins. As to their age and mono- or polygenesis it has been considered that they must be of a different age and such a kind of granular quartz deposits are characteristic for geological settings with a diaphoresis regime and a geotectonic activity, which in this case has been confirmed by earlier local petrological and geotectonic data, as by comparison with similar quartz deposits in other places.

Conclusion

Paramagnetic hole centers in quartz are a useful tool for distinguishing of different genetic types of granular vein quartz. Specific lines in the EPR spectra can be used for quality estimation, quartz purity and grade for industrial purposes.

Paramagnetic hole centers with specific lines in the EPR-spectra at $g=2.049$, 2.034 and 2.022 are supposed to be a typical for granular quartz set of centers.

Hole centers are with a higher concentration in the quartz samples from the granitoids, compared to samples from metamorphic host rocks. In a certain deposit or quartz vein the hole center concentration is lowest in milky-white non-contaminated quartz samples.

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