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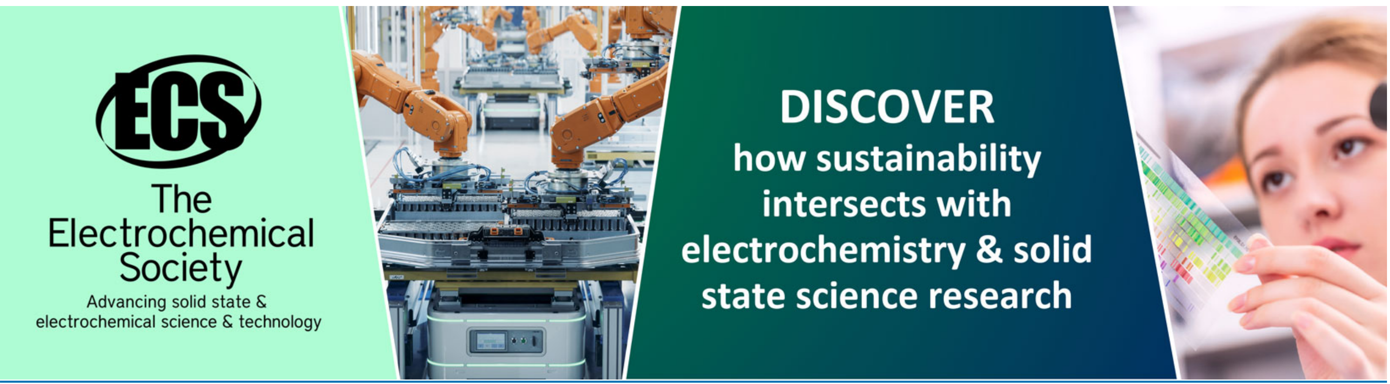

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Relationship of Technological Properties with Dynamic Recrystallization of Quartz on the Example of Objects of the Karelian-Kola Region

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Abstract. Despite the significant reserves of quartz raw materials, there is a deficit of high purity quartz. It is due to the strict technical requirements imposed by standards for this type of raw materials and technological properties of quartz, which are determined by the features of the crystal structure. The crystalline structure is of particular importance for the technological properties of quartz, since such important characteristics as the limit of raw material enrichment, dissolution rate in acid, melting point of quartz, etc., are determined. The formation of the crystal structure of quartz under natural conditions is associated with the successive dynamic recrystallization of the mineral. The degree of dynamic recrystallization of quartz reflects the distribution of dispersed impurities. If it is weakly manifested, the dispersed impurities are not displaced from one zone to another, and all quartz microblocks contain approximately the same concentration. In this case, more or less uniform dissolution of various regions of quartz is observed, and the pattern of distribution of submicroscopic inhomogeneities is monotonic. If intensive dynamic recrystallization of quartz takes place, then it causes a significant redistribution of the scattered impurities. Then the treatment in HF leads to the appearance of a contrast pattern of the distribution of submicroscopic inhomogeneities. The details of the crystal structure of quartz in this work were investigated by the electron paramagnetic resonance (EPR) method using the ER-420 "Bruker" spectrometer. In the selected samples of quartz, the concentrations of isomorphic impurities Al and Ti were measured, and the degree of crystallinity D of the mineral was estimated from the EPR spectra of each of them. Thus, the technological properties of quartz are determined by various geological processes. The results of the studies show that when evaluating the prospects of quartz raw materials, it is necessary to take into account the staged dynamic dynamical recrystallization of quartz in natural conditions. This factor can play both a positive and a negative role at various stages of mineral formation. Its influence is reflected in the state of the crystal structure of quartz, which should be taken into account when developing effective technologies for its enrichment. The intermediate stage of dynamic recrystallization corresponding to the end of the second stage-the beginning of the third stage of quartz recrystallization-is optimal for the formation of high-purity quartz. When choosing a site for the first-stage quartz mining at large deposits in the Karelian-Kola region, one should be guided by the stage of dynamic recrystallization.

1. Introduction

The features of the crystal structure of quartz are important for the technology of its enrichment and should be taken into account in evaluating the prospects of quartz raw materials. This conclusion follows from an analysis of the processes taking place in natural quartz during its geological history.

It is known that the formation of the crystal structure of quartz under natural conditions is associated with the successive dynamic recrystallization of the mineral at high temperatures and pressures. It leads to the removal of mechanical stresses in quartz by replacing deformed grains with new, undeformed ones. As a result, crystallites of quartz with a more perfect crystalline structure are formed, and the total degree of crystallinity of the mineral increases.

Three degrees of dynamic recrystallization of quartz can be distinguished, differing in the mechanisms of their realization [1]. The first stage is carried out at temperatures T = 250-400ºC and is associated with local movement (extrusion) of the boundaries of defective quartz microblocks and the formation of less deformed grains (the mechanism BLG - from English "bulging"). The second stage, which proceeds at T = 400-500ºC, leads to the rotation of some parts of the quartz microblocks relative to others and the appearance of more perfect grains (the mechanism SGR - "subgrain rotation"). The third stage is realized at T> 500ºC and causes a high-temperature migration of grain boundaries GBM - "grain boundary migration".

Simultaneously with the rearrangement of the crystal structure of quartz, the shape of the presence of atoms of dispersed impurities changes in it. Initially, they concentrate near point defects, dislocations, pores, cracks and are separated from each other. With dynamic recrystallization impurities are forced into the defect zones, where they acquire high diffusion mobility and the ability to interact with each other and with quartz crystallites. When introduced into crystallites, impurity atoms are forced to occupy positions in the crystal lattice; The number of structural disturbances in quartz, where they can localize, sharply decreases. Therefore, the regular result of recrystallization is an increase in the amount of isomorphic impurities in the mineral.

Thus, dynamic recrystallization stimulates the development of processes that affect the technological properties of quartz differently. On the one hand, it contributes to its purification and the formation of areas of perfect crystal structure. At that, the atoms of dispersed impurities are concentrated in the defect zones, where they become accessible for leaching. On the other hand, dynamic recrystallization leads to enrichment of quartz with isomorphic impurities. This process is especially active in the third stage of recrystallization, when the atoms of dispersed impurities begin to intensively penetrate into the quartz crystallites. Simultaneously, a decrease in the degree of crystallinity of quartz is observed, due to the entry of foreign atoms into the crystal structure.

Consequently, the intermediate stage of dynamic recrystallization is optimal for the formation of quartz of high purity. It provides the greatest degree of crystallinity of quartz and a moderate level of isomorphic impurities. At earlier stages of dynamic recrystallization, quartz is not sufficiently crystallized, and at later stages is excessively enriched by structural impurities. It can be assumed that the optimal stage corresponds to the end of the second - the beginning of the third stage of the dynamic recrystallization of quartz.

2. Objects and methods

Based on the above provisions, quartz studies of several deposits and ore occurrences of the Karelian-Kola region have been carried out. The present research was aimed at supplementing the results obtained earlier with new data on the structural characteristics of quartz, which are of technological importance [2, 3].

Structural characteristics of natural quartz are closely related to its genesis and can be used to study the conditions for the formation of mineral deposits [4, 5, 6, 7]. It is known that the distribution of the concentrations of isomorphic impurities in quartz, measured by electron paramagnetic resonance (EPR), bears information about the stages of ore formation, the degree of closeness of mineral formation systems, the formational affiliation of ore deposits, and so on.

Table 1. Structural characteristics of quartz raw materials of some investigated objects

Deposit	Variety of quartz	Number of standards	N_{Al}, ppm	N_{Ti}, ppm	D
Fenkina Lampi	Veined quartz, milky white	16	$\frac{6.5 \div 22}{11}$	<0.1	$\frac{0.51 \div 0.31}{0.40}$
Melomais	Veined	10	$\frac{6.5 \div 12}{9.0}$	<0.1	$\frac{0.59 \div 0.39}{0.51}$
Rukhnavolok	Veined, recrystallized	4	$\frac{8.5 \div 41}{20}$	$\frac{0.9 \div 3.8}{2.4}$	$\frac{0.72 \div 0.60}{0.64}$
Stepanovo Lake	Fused quartzite	8	$\frac{6.5 \div 8.5}{7.0}$	$\frac{<0.1 \div 1.2}{0.3}$	$\frac{0.53 \div 0.31}{0.44}$

Note: N_{Al} and N_{Ti} are concentrations of isomorphic admixtures of Al and Ti, D is a cristallinity of mineral.

To obtain highly pure concentrates, quartz raw materials should be characterized by minimum values of N_{Al} and N_{Ti} and a maximum value of D.

Despite the substantial inconsistency in understanding that the fundamental aspects of this phenomenon are not completely resolved. One of them concerns an experimental proof of the existence of mobile impurities in quartz.

In the mechanism of isomorphism proposed in [6, 8], mobile impurities have a special role. It assumes that the crystal lattice of quartz can be enriched with impurities of Al, Ti and Ge and after the process of crystallization of the mineral. This hypothesis is based on the results of experimental studies, as a result of which it was established that the thermal action on quartz can lead to a massive introduction of atoms of nonstructural impurities into the crystal lattice of the mineral. At the same time, studying the kinetics of the implantation process showed that their intake comes from regions where the impurity atoms freely move in space. In this connection, it was suggested that in the quartz there are defect zones, where mobile impurities can be concentrated in large quantities.

The existence of mobile impurities in quartz is indirectly confirmed by the data of the analysis of aqueous extracts by the ICP MS method performed in [9]. However, direct evidence of their presence in the mineral has not yet been cited. To confirm the presence of mobile impurities in quartz with the evaluation of their compositions and forms of finding in the mineral, zones of structural inhomogeneity of quartz and the region of impurity accumulation were studied using precision electron microscopy and EPR methods.

To study the macroimpurities in quartz of different genesis, a complex of standard optical-mineralogical capabilities of the POLAM R-211 polarization microscope was used. Investigations of microimpurities in quartz were carried out by transmission electron microscopy (TEM) using the Technai-12 TWIN installation at a voltage of 100 kW. Elemental composition of mobile impurities was determined using an energy dispersive spectrometer "Inka 4", built into the microscope. The spectrometer resolution reached 120 eV. When studying the processes of crack formation in quartz, the scanning electron microscopy (SEM) method was used. The investigations were carried out using the "Tesla" microscope BS-301. A study of the behavior of isomorphic impurities in selected quartz samples was carried out using an EPR "ER-420" ("Bruker") spectrometer. The error in the results of measurements of the concentration of isomorphic impurities Al, Ti and Ge in quartz, on average, was 15%.

3. Results and discussion

Investigations of quartz samples made it possible to detect a number of characteristic zones in which mobile impurities are concentrated. After the action of the intense electron beam, the impurities in these regions undergo a redistribution detected by the TEM method. Behavior of mobile impurities in this case demonstrates an amazing diversity.

Coagulation of mobile impurities in localization zones. The microphotographs in Figure 1 show how mobile impurities and the crystal structure of quartz from the muscovite quartzites of the Mezhozernoye deposit behave under the influence of an electron beam of a microscope. The quartz zone, initially not containing visible impurities (Figure 1a), was characterized by a high degree of defectiveness (Figure 1b). Intensive irradiation with electrons led to the formation of large precipitates of impurities in the investigated zone (Figure 1c) and the ordering of its crystal structure (Figure 1d).

The obtained results indicate that in the given zone some quantity of mobile impurities, located in the form of individual atoms or molecules, was initially localized. Electron irradiation stimulated the process of their coagulation, as a result of which previously indistinguishable atoms or molecules were transformed into particles accessible for observation by the TEM method.

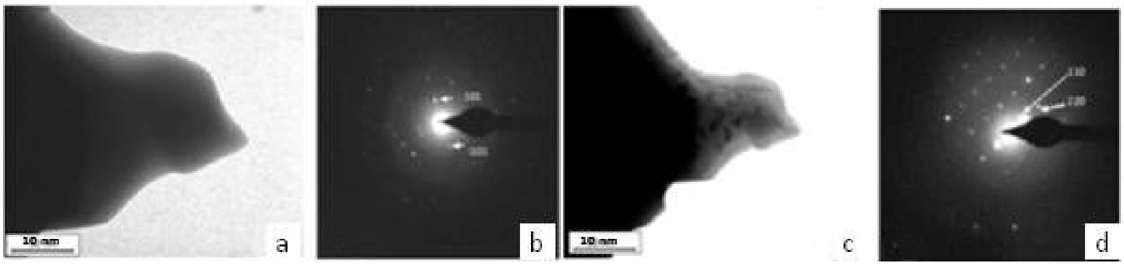

Figure 1. Electronic photomicrographs (in transmitted electrons) of a quartz suspension of muscovite quartzite from the Mezhozernoe deposit: a - obtained at the initial stage of studying it by the TEM method; c - after the presence of the mineral in a focused electron beam for 30 seconds. Microdiffraction patterns of the same sample, corresponding to its initial state and state after irradiation with an electron beam, are presented in fragments (b) and (d), respectively.

A similar behavior of mobile impurities was observed in quartz samples from the quartz-vein deposit Melomaise and quartz of ceramic pegmatites from the Kyuryala deposit, etc. Using the energy dispersive spectrometer, the composition of these impurities was established. It turned out that a whole group of impurities, primarily Fe, Al, Au and Hg, participates in the coagulation processes.

Inversion processes involving mobile impurities. The essence of inversion transitions is that after coagulation of mobile impurities and the formation of large dispersion particles, the reverse process takes place - the decay of large particles into small particles. Moreover, the direct and inverse processes are accompanied by an increase or decrease in the defectiveness of the crystal structure of quartz, respectively.

Inversion transitions were recorded by us within the boundaries of the same regions of defectiveness of quartz samples at different observation times. First, a direct process appears, causing structural changes similar to those shown in Figure 1. Then, after the repeated irradiation of the defective areas by the focused electron beam, the reverse process proceeds. In many cases, inversion transitions are observed without the use of focused electron irradiation, in the regime of continuous observation.

The participation of mobile impurities in the formation of mineral inclusions. The results of the studies show that coagulation of mobile impurities in damper zones can lead to the formation of minerals. Evidence is provided by the data obtained in the study of partially granulated quartz from the quartz vein in the schistostite shales of the Bolshie Keivy (Bollurtian quartz-vortex field, Kola Peninsula).

Figure 2a shows an electron micrograph of this quartz sample. It shows damping zones, some of which contain mobile impurities that have undergone coagulation, while the other part is free of them. In this case, all the damper zones are located in the depth of the quartz grain, where impurities cannot penetrate from the external space. Therefore, the appearance of any particles in the damper zones can be explained only by the processes of interaction of mobile impurities with each other during geological time.

When considering one of the damper zones in Figure 2a we have seen a mineral precipitate, which stands out among other particles in its dimensions. The area of its localization is indicated in the figure by a circle, and the selection itself is indicated by an arrow. An analysis of the microdiffraction pattern of this precipitation (Figure 2b) and the X-ray characteristic spectrum of the impurities contained in this region of quartz (Figure 2c) show that it is nothing more than rutile.

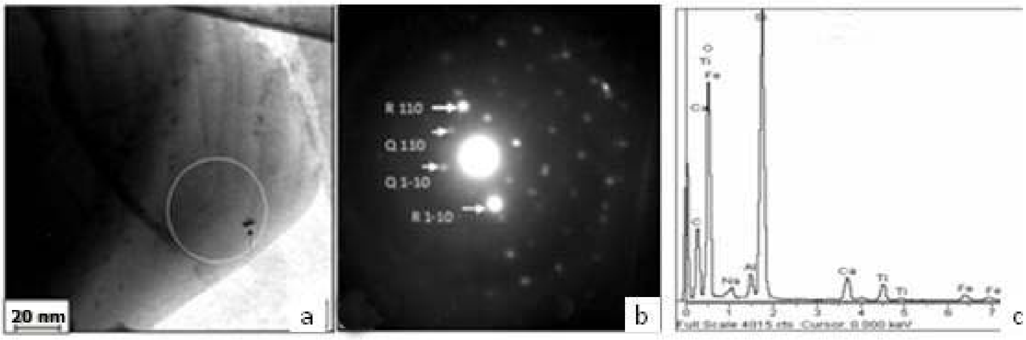

Figure 2. Formation of rutile in the zone of concentration of mobile impurities in a quartz sample from a quartz vein in chiastolite shales. Bolshie Keivy (Kola Peninsula): a - electron micrograph (in transmitted electrons) of a quartz suspension preparation (the arrow indicates elongated rutile release, circle - zone Excitation in microanalysis); b - microdiffraction of quartz (Q) and isolation of rutile (R); c - is the X-ray characteristic spectrum of the impurities.

This result allows us to assume that the rutile needles, which are sometimes observed in veined quartz, can be formed not by its crystallization, but due to the transformation of mobile impurities Ti during the overgrowth of the damper zones.

Movable impurities in the interblock space. An example of a sample with a low content of mobile impurities is quartz from the Maiskoye gold deposit, Karelia. Its crystal structure almost does not change under electron irradiation. By the TEM method, even overgrown damper zones are not found in it.

In some of the most contaminated areas of this quartz (Figure 3a), it was possible to detect coagulation of mobile impurities under the action of an electron beam (Figure 3c). At the same time, the defectiveness of the crystal structure of the mineral did not decrease, as in other quartz, but increased. If the microdiffraction pattern for the initial sample contained weak line kikuchi (Figure 3b), then after irradiation with an electron beam, the kikuchi lines were blurred (Figure 3d). The very picture of microdiffraction retained sufficiently distinct diffraction maxima.

This behavior of microdiffraction allows us to assume that the appearance of coagulated particles leads to a spatial misorientation of microblocks of quartz with the formation of small-angle boundaries between them. The composition of mobile impurities coagulating in this quartz is unstable and very limited. Of these, Fe has the highest concentration. In smaller quantities and much less often there are Al, Au, Co, S and other elements. As we see, with a low content of mobile impurities in quartz, the number of damper zones is small, and the boundary between microblocks is the preferred place of their localization.

Connection of mobile impurities with cracks and micropores. Quartz from the Maiskoye field is characterized by anomalously high brittleness. As was shown in [10], annealing at a temperature of T = 600°C causes the formation of a large number of cracks in it, leading to the destruction of the mineral, even with a weak mechanical action.

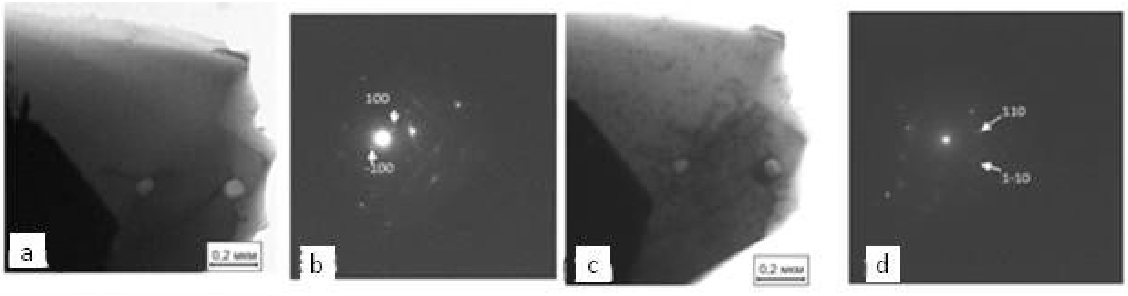

Figure 3. Electronic photomicrographs (in transmitted electrons) of the suspension gold quartz preparation from the Maiskoe deposit: a - for the initial state of the sample; c - after irradiation with an electron beam for 30 seconds. Microdiffraction patterns of the same sample, corresponding to its initial state and state after irradiation with an electron beam, are presented in fragments (b) and (d), respectively

Our investigations have made it possible to determine the cause of the formation of these cracks. The SEM method in quartz from the Mayskoye deposit revealed the presence of two quartz generations. One of them in the photomicrography in the reflected electrons corresponds to quartz regions with a conchoidal fracture (Figure 4a), the other - sections with a sugar-like surface (Figure 4b). Each of the generations is characterized by a large and different number of micropores. The results obtained are consistent with the conclusion of [11] that the formation of quartz veins in the Maiskoye deposit occurred with the participation of two types of fluids - low and high gas saturation. It was found that the appearance in quartz of a large number of cracks and dislocations during annealing is due to the presence of micropores. On the micrograph of Figure 1c can be seen that many dislocations that have arisen in a quartz with a conchoidal fracture pass through micropores, which, apparently, provoked their formation. In quartz with a sugar surface, where the concentration of micropores is particularly large, after annealing at T = 600 ° C, cracks appear (Figure 4d).

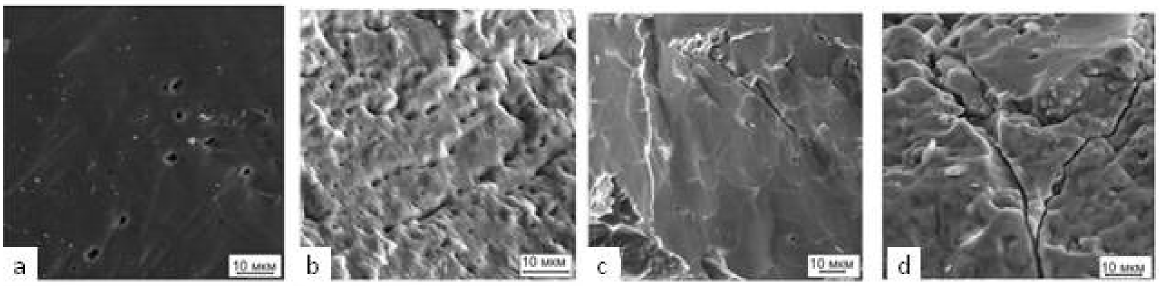

Figure 4. Marskoe deposit quartz generation: a, c - areas with a conchoidal fracture; b, d - section with a sugar surface

The obtained data are consistent with the results of studying quartz by the TEM method. From the consideration of the microphotographs in Fig. 3a and 3c it is clear that micropores are sources of crack formation. These cracks have the appearance of dark bands developing from micropores to the depth of quartz. They serve as an effective drain for mobile impurities. This is evidenced by the accumulation of impurities in the immediate vicinity of the cracks.

4. Conclusion

The data of quartz studies by electron microscopy and EPR methods make it possible to formulate a number of propositions concerning the forms of existence of mobile impurities in quartz, the zones of their localization and the influence on the properties of the mineral.

Areas of localization of mobile impurities in quartz. The obtained results show that mobile impurities in quartz exist and are concentrated in those regions where their active diffusion is possible. The overwhelming part of the mobile impurities is localized in the regions of quartz of high defectiveness. From this it follows that the main carrier of mobile impurities is a weekly crystallized quartz. This conclusion should be taken into account when searching for and developing structural criteria for estimating the prospects of quartz raw materials.

Elemental composition of mobile impurities. The conducted studies have shown that the determination of the composition of mobile impurities in quartz involves a rather difficult problem. In this connection, the results of an analysis performed in [9] are of interest. The technique developed in it has a sensitivity threshold for the most important impurity elements in quartz, close to 10-6%. This is 4-5 orders of magnitude lower than the sensitivity threshold of the energy-dispersive analysis used in our studies. The application of this technique made it possible to establish that when the quartz is crushed into the extract, first of all, Al, Ti, Ga, Sc, Zr, Y and Ge impurities enter. The list of these elements is very revealing. All of them belong to the second and third groups of the periodic table and are similar in atomic characteristics to the Si atom. It can be assumed that their concentration in the damper zones is due to the fact that they are able to replace Si atoms better than other elements.

Of the listed elements, Al and Ti are present in the largest amount in quartz, which can have a decisive influence on the purity of quartz raw materials.

The concentration of mobile impurities in quartz. Movable impurities in defective zones of quartz are part of the dispersed impurities in the mineral. The other part of this form of impurities is isomorphic impurities in the crystal structure. However, the concentration of the latter is several times lower than the content of mobile impurities. Therefore, the presence of mobile impurities should be considered an important qualitative indicator of quartz raw materials, and their elimination is regarded as one of the most important problems of quartz enrichment.

"Dangerous" feature of mobile impurities. Movable impurities in areas of non-crystallized silica at elevated temperatures have an exceptional diffusion activity. It promotes the rapid penetration of mobile impurities into the crystal structure during the heat treatment of quartz during its technological redistribution. Having occupied structural positions in the mineral lattice, the impurities become inaccessible for their removal from quartz. This is their "dangerous" feature for the process of enriching quartz. When developing new technologies, one should take it into account and avoid enrichment of quartz with isomorphic impurities when exposed to temperature.

Connection of mobile impurities with the degree of crystallinity of quartz. The content of mobile impurities plays the role of a regulator of the processes of structural transformations occurring in defective regions of quartz. In regions where there is coagulation of mobile impurities, the formation of a more perfect quartz is noted. Conversely, if the mobile impurities are dispersed, the crystal structure becomes defective. As a result, mobile impurities act as a factor determining the degree of crystallinity of quartz.

This regularity must be taken into account when predicting the technological properties of quartz raw materials, in particular, its behavior in high-temperature chlorination. Effect of energy on mobile impurities in quartz. It is established that different types of energy influence cause unequal behavior of mobile impurities in quartz and, as a consequence, the state of its crystal structure. Radiation irradiation leads to the dispersion of mobile impurities and the formation of a less perfect crystal structure of quartz. Thermal warming, on the contrary, simulates their coagulation and the emergence of an ordered structure. The combination of various types of energy impact can be used in technological processes to regulate the state of the crystal structure of quartz and to achieve optimal conditions for the removal of mobile impurities.

Movable impurities and fissuring in quartz. During the research it was shown that the abundance of mobile impurities increases the quartz's resistance to mechanical destruction, and their lack can cause excessive brittleness of the mineral. The latter property is due to the appearance of cracks in the mineral, as evidenced by the data on the study of quartz at the Maiskoye deposit. The result obtained is of great importance for the explanation of the mechanical properties of quartz and their possible changes in the processes of its technological redistribution.

References

[1] Dynamic recrystallization of quartz: correlation between natural and experimental conditions. M Stipp, H Stuitzк, R. Hellbraunner, S. Schmid. 2002 p 171-190.
[2] Movable impurities in the quartz of the Karelo-Kola region. L.T.Rakov, V.T. Dubinchuk, L.S. Skamnitskaya, V.V. Shchiptsov // Proceedings of the Karelian Scientific Center of the Russian Academy of Sciences (series "Geology of the Precambrian"), No. 10, 2016. - P.100-118.
[3] L.T.Rakov, V.V. Shchiptsov, V.T. Dubinchuk, L.S. Skamnitskaya Quartz raw materials of the Karelian-Kola region: the nature of formation and the genetic significance of submicroscopic structural inhomogeneities in quartz // Proceedings of Kar. SC RAS. 2015. № 7. P. 164-180.
[4] E.I. Dolomanova, L.V. Bershov, M.S. Gasoyan Isomorphic elements-impurities in vein quartz of tin ore deposits of the Transbaikal and their genetic significance // Proceedings of the USSR Academy of Sciences. - 1972. - № 6. - P. 65-74.
[5] V.P. Lyutoev, Yu.V Glukhov., V.P. Suetin, A.Yu. Lysyuk, B.A. Ostashchenko, M.F. Samotolkova Spectroscopy of impurity defects in minerals from endogenous and exogenous objects: structural impurities and adsorbed molecules as markers of geological processes. Syktyvkar: Geoprint. 2007. 44 pp. (Report Series No. 5 (54).
[6] L.T.Rakov, T.N. Shuriga Structural-dynamic state as a genetic criterion of quartz // Geochemistry. 2009. № 10. P. 1086-1102.
[7] Shchiptsov V.V., Scamnitskaya L.S, Voytekhovsky Yu.L., Bubnova T.P.Dubinchuk V.T., Rakov L.T. Geological and mineralogical-technological appraisal of quartz as a raw material from the Karelia-Kola quartz-bearing province, a new promising region of Russia // Abstracts and Proceedings of the Geological Society of Norway. The Arctic Days 2014. Norsk Geologisk Forening c/o Norges geologiske undersokelse N-7491 Trondheim. P.80-81.
[8] L.T.Rakov Mechanisms of isomorphism in quartz // Geochemistry. 2006. № 10. P. 1085-1096.
[9] S.G. Kryazhev, V.Yu. Prokofiev, Yu.V.Vasyuta The use of the ICP MS method in analyzing the composition of ore-forming fluids // Vestn. Moscow. University. Ser. 4. Geology. 2006. № 4. Pp. 30-36.
[10] L.S. Skamnitskaya, T.P. Bubnova Influence of the heat treatment method on the physicochemical properties of the quartz of the Mayskoe deposit // A collection of articles on the materials of the reports of the VIII Russian Seminar "Technological Mineralogy in Optimizing the Processes of Mineral Preparation and Enrichment of Mineral Raw Materials" Petrozavodsk: KarRC RAS, 2014. P. 124-132.
[11] A.A. Wolfson Geological and genetic features of the gold-quartz deposit "Maiskoe" (North Karelia): the dissertation of the candidate of geological and mineralogical sciences. M., 2004. 165 pp.