EXTRACTION OF CRISTOBALITE FROM MILKY–WHITE FORMS OF QUARTZ STUFF[1]

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1. INTRODUCTION

Natural quartz is one of the main sources of getting a unique material - quartz glass. Wide application of quartz glass in chemical and electronic industry, aviation and cosmonautics, fibre optics and computer techniques makes it absolutely indispensable. However, industrial reserves of rock-chrystal lodes, that is the most pure source of quartz stuff with minimal mineral admixturer, are practically exhausted everywhere. All this results in usage of low quality stuff and, thus, to significant complication of technological schemes of quartz processing and concentration, to high energy waste, high waste of inorganic acids, significant increase of industrial waste. Quartz concentrate output according to traditional technologies of lode quartz processing on Urals deposits is not more then 35%. In this turn the part of defectless transparent quartz glass when smelting from granular quartz is not more then 30%. It is evident that low efficiency of quartz industry call to new scale technological decisions.

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2. MAIN MODERN TECHNOLOGICAL TRENDS IN PRODUCTION OF PURE SILICA

Pure silica is mainly used in production of transparent and multicomponent quartz glass, the most deficient in volumes and quality of the used quartz. Nowadays, the main technological trends in this field come to processing of various natural types of quartz (rock crystal, crystalline, glassy, granulated and milky-white) and to synthesis of silica tetrachloride ($SiCl_4$).

Modern technological schemes of natural lode quartz processing are based on a complex of concentration processes: hand and automatic sorting, crushing, chemical processing in inorganic acids, pounding, flotation, electroseparation, magnetic separation. There are two traditional trends: the first one is making of industrial production on concentrating mills with their further retreating on glass plants; the second one is making of quartz concentrates on ore mining and processing enterprises suitable for smelting of quartz glass.

Now the resources of piezoquartz (rock crystal formations) in Russia are practically exhausted, there is also significant shortage of tykoquartz (quartz with concentration of SiO_2 not less then 99,98 %) suitable for smelting of transparent quartz glass. Thus, other types of quartz stuff are being processed: glassy, granulated, milky-white. However, traditional technological processes of preparation and processing these types of quartz do not provide the final product of high degree of purity, so that the sum of impurities would not be more then 10^{-4}%. So, in our practice making of transparent quartz glass out of natural quartz for the needs of cosmonautics, aviation, laser, nuclear, satellite technique, electronic and chemical industry, fibre optics remains rather problematic.

Basically different source for making of quartz glass is silica volatile components - mainly $SiCl_4$. Chemical technologies of making quartz glass are based on high temperature vapourphase synthesis from silica tetrachloride ($SiCl_4$) in hydrogenic-oxygenic flame by reaction:

$$SiCl_4 + H_2O \rightarrow SiO_2 + 4HCl \qquad (1)$$

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or by oxidizing of silica tetrachloride in oxygenic low temperature plasma by reaction:

$$SiCl_4 + O_2 \rightarrow SiO_2 + Cl_2 \qquad (2)$$

Ecological problems bound with such production are due to harmful effects of the large emitted volumes of chloride combinations HCl and Cl_2 and the necessity to trap them. In particular, 5 - 6 kg HCl (!) are being emitted for each kilogram of the smelt glass, the losses of silica tetrachloride being 50% (!) (V. P. Pryanyshnikov, 1971).

But for the enumerated drawbacks presenting certain ecological threat, tetrachloride technologies are not perfect as far as the quality of the end product is concerned. The smelt glass has significant amount of hydroxyl groups (OH) which provoke an intense range of absorption 2720 nm, and the reduced heat-resistance. Glass obtained by means of hydroxyl-free technology has considerable amount of Cl (up to 0,05 %), common demands to the sum of impurities being $\leq 1{,}10^4$ % (V. K. Leko, O. V. Mazurin, 1985).

So, chemical methods of making artifical silica could not be accounted as satisfactory and optimal for the development of quartz production. They aggravate ecological problems and only to a certain extent solve the problem of providing the quartz stuff for glass industry. In essence, there was "frozen" large production resources bound with extraction and processing of quartz (in particular, deposits and concentrating mills of the Urals), and aggravated the problems of employment.

3. TECHNOLOGICAL PRINCIPLES OF DEEP PURIFICATION OF MILK-WHITE QUARTZ OFF GAS-LIQUID IMPURITIES

Among various types of crystalline quartz stuff the most promising for the high-quality transparent quartz glass are milk-white modifications of quartz (for example, from deposits "Dodo", "Mountain Krustalnaya", "Novotroitskoye" - Russia, "Aktas" - Kazakhstan). The content of mineral admixtures in some of milk-white quartz varieties is not less than in rock-glass (Table 1) (V.I.Yakshin, 1976).

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Table 1

Main physical parameters of various types of quartz

No	Type of quartz	Light trans-mitting T, %	Calci-nation losses, %	The amount of gas-liquid impurities (cm³ for each 1000 grains of quartz)	Water para-meter H_2O, CO_2	The amount of mineral impurities (n-sing for each 1000 grains of quartz)	The elemen-tary cell volume (A³)	The rate of solu-tion in HF (%/hour)	Ab-sor-ption in IRS (q)
1.	Rock crystal	60 - 95	0,001 - 0,02	1 - 10	1 - 4	0 - 10	112,913	0,08	0,13
2.	Milky-white	10 - 30	0,03 - 0,05	35 - 60	4 - 10	0 - 5	112,950	1,5	no infor-mation
3.	Glassy	20 - 60	0,02 - 0,04	10 - 30	2 - 5	2 - 25	112,949	0,68	0,36
4.	Granu-lated	50 - 90	0,02 - 0,05	4 - 10	1 - 2	3 - 20	112,923	0,16	0,15

It might be well pointed that milk-white quartz supplies in Russia (the Urals), Kazakhstan (Aktas), Brasilia (Mimoso, Shiki-Shiki, Cety-Lagoas, Cristallina), Madagascar (Manakara, Itermo), Angola (Pokarisa) are practically unlimited and add up to billion tons. The only technological limit to wide milk-white quartz deposits exploitation is high content of gas-liquid impurities in them (GLI), the disposal of which by traditional means is not effective.

The known methods of GLI disposal from quartz are as follows: mechanical - that is grinding providing breakdown of caverns, channels and pores; and thermal - that is thermoprocessing of line-grained and mean-grained quartz fractions in the range of temperatures 440 - 600 °C (deposits of the Middle Urals and Bashkiria), or 900 - 1100 °C (deposits of the Middle Urals). However, the investigations of the milk-white quartz varieties has shown that they are characterized by ultra small dimensions of GLI, mean area of which varies from 2,6 up to 30,0 x 10^{-6} mm^2 depending on a deposit (V. A. Issaev, V. T. Dubinchook, 1997). Such impurities could not be revealed by common thermoprocessing.

New approach of the extraction of GLI from quartz (Author's certificate N 1818309) is based on the process of its modified

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transmitting into low-temperature crystobalite (α - crystobalite) according to the scheme (Fig.1).

Fig. 1

The scheme of polymorphous transfer of quartz into low - temperature crystobalite

heating to T=1650 - 1700 °C + endurance 30 - 60 мин →			cooling to T<250 °C →
573°	**870°**	**1470°**	**250 - 280 °C**

α - quartz → β - quartz → tridymite (S_4) → β - crystobalit → α - crystobalit

The stated consequence of polymorphous conversion for each pair of the neighboring quartz modifications in this row is followed by significant change of elementary cell volume by 0,6% (K. S. Filatov, 1990). β - quartz → tridymite - by 4%, tridymite → β - crystobalite - by 5 - 6%, and, correspondingly, conversion of β → α - crystobalite is attended by the decrease of elementary cell volume by 5,6% (V. P. Pryanashnikov, 1971). So, modified thermoprocessing of quartz up to α - crystobalite through multiple meaning changes of elementary cell volume leads to revelation of even small GLI.

However, it is necessary to state that polymorphous transfers of quartz into tridymite and of β - crystobalite are effective only if there are modifying admixtures. Modifying admixture are mainly alkaline elements, their sum being not less than 10^{-3}%. For quartz stuff of milk-white variety of the Middle and SubPolar Urals deposits the content of admixture elements varies within the limits of $(70 \div 350)10^{-4}$%, the alkaline elements admixture Na and K is $(10 \div 80) \cdot 10^{-4}$%. The mentioned types of the quartz stuff are suitable for modification thermoprocessing aimed at production of GLI-free silica in the form of α - crystobalite.

4. EXPERIMENTAL STUDIES OF QUARTZ CRYSTOBALIZATION

The carried out investigations of various milk-white varieties have shown that traditional thermoprocessing do not provide effective results of GLI purification irrespective of temperature and rate of heating. There are several reasons to it, first, because of the quartz granules smelting while GLI are being removed. Second, the temperature of quartz granules treatment under the known technologies conditions (USA patent N. 3565595, 1971) varies in a wide range from 1500°C and up to temperature higher than the point of phase transfer of α - quartz into β - crystobalite. All this do not allow to count on a full removal of GLI. Purification of milk-white quartz from GLI is conditioned by revelation of both microscopic and macrocavities filled by gaseous and liquid admixtures resulting from the transfer of α - quartz into β - crystobalite in temperature interval of 1470 up to 1723°C according to Day-Sorsman scale. It was experimentally stated that the crystobalite content in thermoprocessing of quartz stuff grows quicker, the higher is temperature. For example, the time of heating being 0,5 hour and temperature 1600, 1650 and 1700°C the output of crystobalite is 0, 50 and 80% correspondingly for the quartz stuff with mean grains diameter 0,5 mm. The dimension of grains of thermoprocessed material is an important factor influencing the effectivity of quartz-crystobalization process. It was stated that the diameter of grains being increased up to 70 mm, the yield of crystobalite also increases when compared with the previous experiments and is 48,82 and 98% correspondingly. The analysis of the results of twenty experiments on crystobalization of quartz of various granulometric composition has shown that the maximum yield of crystobalite is not more than 80% for grains less than 2,5 mm at various temperature-temporal regimes.

Fig. 2 shows the dependence of the influence of grain size of the initial quartz (deposit "Aktas", III generation) upon the yield of crystobalite depending on temperature of thermoprocessing.

The experiments have shown that thermoprocessing of milk-white quartz at 1600°C has low output of crystobalite (not more than 45%), and the increase of the time of heating sharply decreases the capacity of the process and is not profitable. The most optimal temperature interval for quartz stuff processing is 1650 - 1700°C. The rate of crystobalization at such temperatures is maximum, the time of heating is not more than 1 hour.

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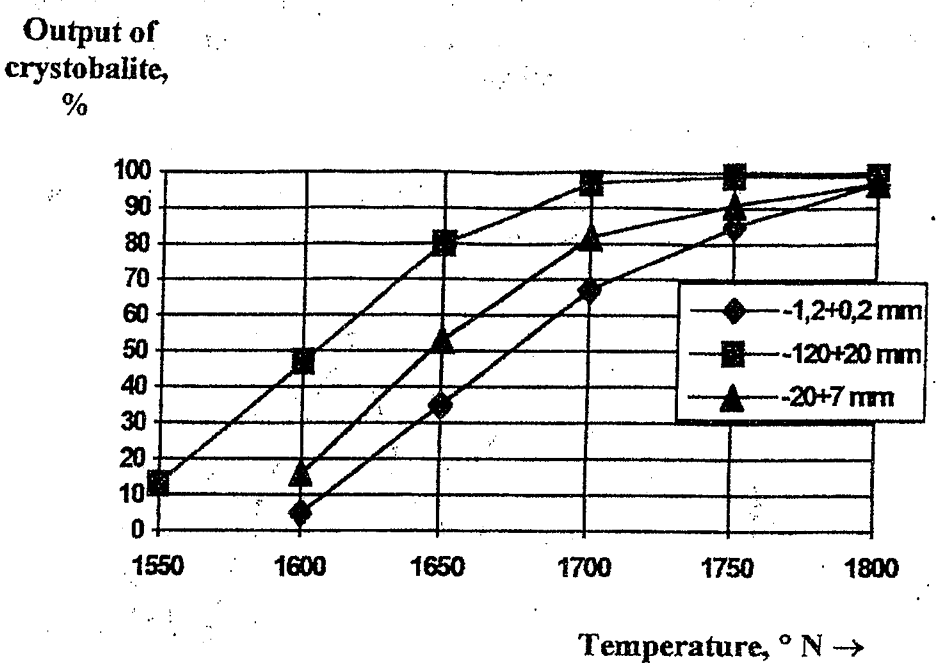
The influence of grain size of milk-white quartz upon the yield of crystobalit depending on temperature processing



(Time of thermal treatment 0,5 h)

Fig. 2

The increase of temperature of thermoprocessing of the quartz stuff for more than 1700°C is not expedient, because of crystobalite melting down which disturbs the quality of the product and hinders its further dressing off mineral impurities. The temperature at which crystobalite fully transfers into fusion is 1723°C. It was experimentally stated that the larger is the grain, the higher is crystallite content in the processed quartz stuff, and, consequently, the more effective in the process of GLI removal.

Fig. 3 shows the ratio of the influence of mean diameter of grains upon the glass phase formation. These ration testifies to the decrease of temperature of crystobalite smelting with the decrease of grains dimensions.

It was stated that the influence of grain size upon intensification of crystobalization process is due to the character of GLI spreading in the mass of quartz stuff on different preliminary stages. Thus, the crushed

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and fractured quartz granules (grain diameter: 0,1 - 0,4 mm) is partly released from those gas and liquid impurities which concentrate along the surface of the healed cracks of crystals and, consequently, the amount of impurities containing mainly Na^+ and K^+ ions lessens, which in its part decreases the rate of crystobalization.

The influence of grain size of milk-white quartz upon the amount of the glass phase

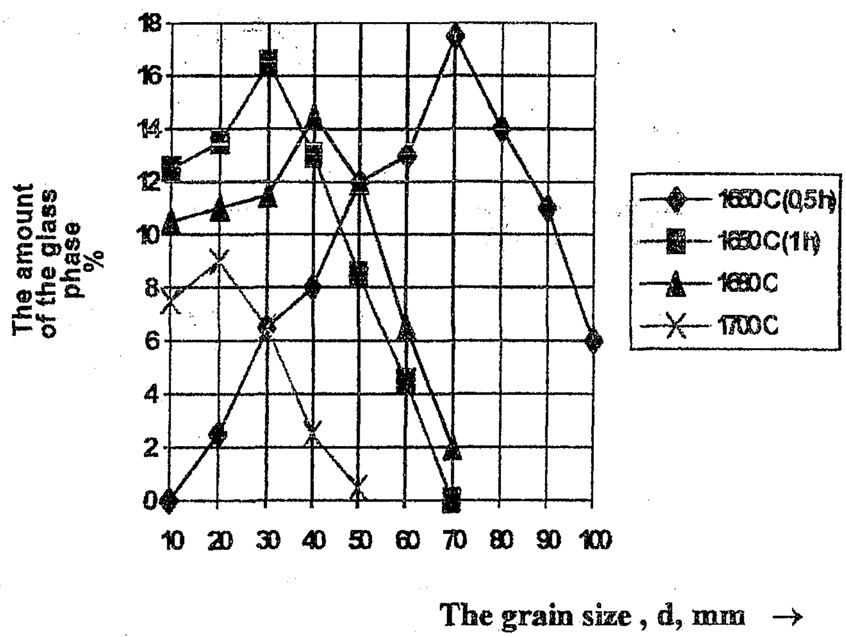

Fig. 3

With the growth of mean dimensions of grains especially of the uncrushed and unconcentrated ones, the rate of crystobalization considerably increases, even minute traces of alkaline impurities on the surface of crystals lead to the transfer quartz into crystobalite.

Theoretical and experimental studies allowed to develop method of purification of milk-white quartz gas-liquid impurities (1).

In Table 2 the results are presented of milk-white quartz crystobalization depending on thermoprocessing conditions, grain size and ratio of $\varnothing_{max}/\varnothing_{min}$ fractures diameter.

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5. TECHNOLOGICAL SCHEME OF MILK-WHITE QUARTZ PROCESSING BY MEANS OF MODIFICATIONAL THERMOPROCESSING

On the base of the developed method of milk-white quartz purification from GLI there was developed technological scheme of this type of the stuff processing. It provides production of especially pure silica in a form of crystobalite (Fig. 4). The scheme is based on modified thermoprocessing of the preliminary fractured initial stuff. The peculiarities of this method are as follows:

- The main technological operation is special thermoprocessing of lump or coarse-grain milk-white quartz at 1650 - 1700°C temperatures. The process may be performed in induction or HF-kilns.
- Depending on the amount of the initial product types it may be produced in powder, large-grain or lump crystobalite forms. Powder crystobalite provides making new types of commodities after crushing, preliminary pressing and further transfer into glass.
- Chemical processing is applied only in case of necessity, of the initial stuff do not meet technical requirements (TR).
- Considering chemical processing this method allows to unify all types of quartz stuff.

6. CONCLUSIONS

The analysis of literary data and studies of peculiarities of milk-white quartz stuff varieties under high-temperature processing conditions allowed to justify new method of intransparent varieties of quartz processing. The method allows to produce very pure silica in the form of crystobalite for transparent glass melting.

The proposed method presupposes new means of preparing the initial quartz stuff for the processing, in particular, the application of large and superlarge grain size material (up to 120 mm) (according to traditional technologies the final product-quartz concentrate - should be 0,1 - 0,4 mm which finally leads to considerable decrease of industrial energy losses.

Crystobalite obtained in the result of polymorphous quartz transformation is highly porous and its deep purification may be achieved with better results when compared with quartz granules.

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The proposed method makes it possible to develop technological version of obtaining quartz glass from milk-white quartz during one cycle, that is to combine processing of the inital quartz stuff with quartz glass production.

Table 2

The results of crystobalization of milk-white quartz depending on thermoprocessing conditions, grain size and ratio of fracture diameters

NN experi-ments	Fraction, mm	Φ_{max}/Φ_{min}	Conditions of thermoprocessing		The yield of product after thermoprocessing, %			The degree of gas-liquid impurities disposal
			T, °C	Time, hour	quartz	crysto-balit	the glass phase	
1	-1,2 + 0,2	6	1600	0,5	70	-	30	31,3
2	-1,2 + 0,2	6	1600	1,0	15	48	47	45,8
3	-1,2 + 0,2	6	1700	0,5	5	80	15	84,2
4	-3 + 0,5	6	1680	0,5	7	83	10	81,1
5	-6 + 3	2	1680	0,5	2,0	97	1,0	96,9
6	-9 + 3	3	1680	0,5	2,5	96	1,5	96,61
7	-12 + 3	4	1680	0,5	3,0	95	2,0	94,36
8	-18 + 3	6	1680	0,5	6,0	90,5	3,5	90,4
9	-20 +7	2,8	1650	1,0	8	87	5	89,27
10	-20 + 7	2,8	1680	0,5	2	98	-	97,2
11	-20 + 7	2,8	1730	0,5	-	88	12	96,04
12	-21 + 3	7	1680	0,5	7	88	5	87,0
13	-120 + 20	6	1600	0,5	48	52	-	43,4
14	-120 + 20	6	1650	1,0	4	96	-	94,92
15	-120 + 20	6	1680	0,25	10	85	5	87,57
16	-120 + 20	6	1680	0,5	2	98	-	96,62
17	-120 + 20	6	1680	0,75	3	97	-	97,46
18	-120 + 20	6	1680	1,25	-	96	4	98,3
19	-120 + 20	6	1700	0,5	-	100	-	97,9
20	-120 + 20	6	1700	1,25	-	92	8	96,61

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PRINCIPLE TECHNOLOGICAL SCHEME OF MILK-WHITE QUARTZ PROCESSING

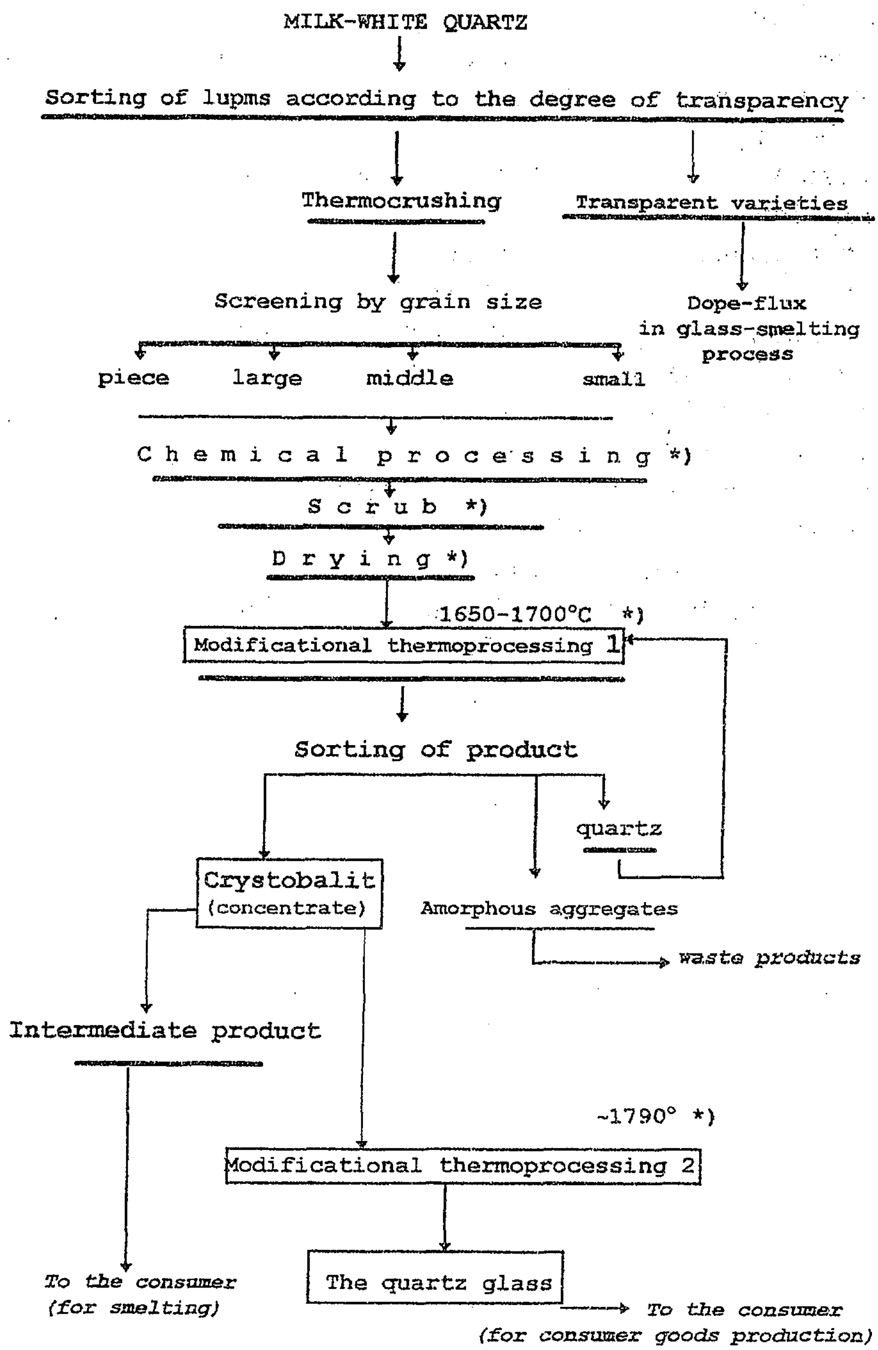

Fig. 4

*) Technological operations are perfomed separately for each class

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References

1. Author's certificate N 1818309 (Russia). The method of purification of quartz. /A. J. Zivoluk, N. G. Oreshnikova, V. A. Issaev, P. D. Starovoitov. Bulletin of inventions, 1993, N 20.
2. The mineralurgy of lode quartz. / Kyshtymski ore mining and processing enterprise. Edited V. G. Kuzmin, B. N. Kravez. - M.: Nauka, 1990. - 294 p.
3. Leko V. K., Mazurin O. V. Relations of quartz glass. - L.: Nauka, 1985. - 166 p
4. Pryanyshnikov V. P. The system of silika. - L.: The publishing literature on building, 1971. - 240 p.
5. Yakshin V. I. Granulated quartz of complex migmatique - stuff optimum for making of quartz glass. / Geology of metamorphyque complex of Urals. - 1976, Number 127.
6. Filatov S. K. High temperature crystallochemistry. Theory, Methods and Results of researchs. - L.: Nedra, 1990. - 288 p.
7. Issaev V. A., Oreshnikova N. G. Examination and quantitative estimation of fluid inclusions in quartz using scanning electron microscope (SEM). Ores and Metals. - N 1. - 1997. - 43 - 49 p.
8. USA Patent N 3565595, 1971.

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