EXPERIMENTAL STUDY OF THE INFLUENCE OF CRYSTALLIZATION CONDITIONS ON CAPTURE AND DISTRIBUTION OF GERMANIUM IN SYNTHETIC QUARTZ

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Key words: *Quartz, germanium oxide, hydrothermal crystal growth, piezoelectricity*

The objective of the investigation was the experimental study of influence of various physico-chemical and growth factors on capture and distribution of germanium in crystals of synthetic quartz. The growth of crystals was carried out by a hydrothermal method of temperature gradient in autoclaves of 280 cm^3 in volume. The aqueous solutions of NaOH, Na_2CO_3 and NH_4F were used as mineralizers. Seed plates and bars of were prepared from synthetic quartz crystals cut parallel to faces of pinacoid {c}, negative {z} and positive {r} rhombohedrons, trigonal prism {x}, hexagonal prism {m} and trigonal dipyramid {s}. The nutrient was prepared from crushed synthetic quartz and powder of germanium oxide (hex) at weight proportions of GeO_2: SiO_2 from 1:20 to 1:2. The crystal growth runs were carried out in absence of a diaphragm with placing of seed plates or bars for all length of an autoclave. That has allowed growing of so-called wedge-like crystals with growth rates from zero to highest possible under the set conditions of growth [1]. Autoclaves were heated in furnaces with two-section electric resistive heaters. The duration of crystal growth runs was from 14 to 30 days. The autogenous pressure was set by aqueous solution filling of autoclaves and defined by with the corresponding P-V-T diagrams for used or similar composition solutions [2]. The temperature control was carried out with the help of chromel-alumel thermocouples and standard thermo-measuring devices with accuracy ± 1°C. The crystal growth runs were realized at temperatures from 270 to 720°C and pressure, accordingly, from 10 – 180 MPa. The difference of temperatures between bottom and top parts of autoclave was from 5 to 30°. The morphology and the internal structure of as grown crystals were studied by binocular (MBS-9) and polarising (Amplival) microscopes. The optical characteristics were defined by the Fedorov's and immersion (index-matching fluid) methods. The content and distribution of silicon and germanium in crystals were determined by the local analysis with use of microprobe CamScan MV2300, MBX with power-dispersive spectrometer Link 860. The unit cell parameters were calculated on the basis of the X-ray powder diffraction patterns obtained on ADP 2-01, Co anode (λ=1,79021 Å). The IR and Raman spectres were registered, accordingly, on spectrometers Anatar FT-IR, Nicollet, and RM1000, Renishaw. The temperature of phase transition was defined on Thermal System DTA TAG 24S16, Sataram.

Crystals of quartz with GeO_2 content from 0.98 to 38.78 weight % have been grown (fig. 1). The morphology of the crystals containing less than 6 weight % of GeO_2 practically does not differ from morphology of the pure quartz crystals which growth in similar conditions. At higher content of germanium the shape of crystals changes through an equalizing of growth rates of both negative (Vz) and positive (Vr) rhombohedrons, and hexagonal prism (Vm). Especially distinctly it is visible on crystals of spontaneous origin, the habit of such crystals changes from prismatic to isometric with wedging-out of faces {m}.

The greatest morphologically stabile forms, of the as grown crystals obtained in all solutions, present by faces of the main rhombohedrons and hexagonal prism though quite often they are exposed to Dauphiné and Brazil law twins. Other faces are unstable and replaced by set of densely adjoining to each other pyramids, formed by faces {r} and {m} (alkaline solutions) and faces {+s}, {+x} and {-x} (fluoride solutions). Thus in growth sectors <c> of the crystals which have been grown in alkaline solutions numerous gas-liquid inclusions are formed. The faces {c}, {+x}, {+s} and {-x} of the quartz crystals grown in fluoride solutions have a rough relief. However under certain conditions their growth sectors keep uniformity in wide range of T-P parameters and growth rates. Another macro defect of germanium contained quartz are cracks which cover basically seed and grown layer adjoining to it.

The maximum content of germanium are marked in growth sectors <c>, <r> and <z>, and minimum – in sector <m>. The growth sectors <+s>, <+x> and <-x> have an intermediate position. Quite often it is observed parasitic sectors of growth and zones with various (to several weight %) content of germanium inside of the growth sectors. The most uniform distribution of germanium is marked in growth sectors <z> and <r> which are not subjected to twining and degeneration. In the growth sector <c> it is observed «striated» character of distribution of germanium connected with the regeneration mechanism of growth of crystals (fig. 1, on the right).

The maximum influence on the content of germanium oxide in quartz is rendered to temperature and growth rate of crystals. Rise in temperature of growth of the crystals which have been obtained at identical growth rates (0.11 mm/day in the direction [0001]) from 400 to 700 °C leads to increase in content of GeO_2 in quartz from 0.98 to 22.3 weights % (alkaline solutions) and from 6.6 to 30.06 weights % (fluoride solutions). In the crystals grown at identical temperature (615°C), but with growth rates of 0.07 and 0.12 mm/day in the direction [0001] content of GeO_2 is, accordingly, 7.02 and 16.39 weight %.

The proof of the structural position of germanium in quartz is the appropriate increase of unit cell parameters as a function of germanium content. For example, the values of the parameters ***a*** and ***c*** equal to 4.9131 and 5.4050 Å, accordingly, for synthetic quartz, increase to the values 4.9233 and 5.4240 Å for the quartz containing 24 weight % of GeO_2. Also, there is an increase of refraction indexes from n_o=1.553 and n_e=1.544 of pure quartz to, accordingly, 1.562 and 1.572 for germanium contained quartz. The IR-spectres of germanium contained quartz, unlike usual quartz, show two new absorption bands with maximums close to 1010 and 930 cm^{-1} and two disappeared absorption bands with maximums at 695 and 513 cm^{-1}. That possibly is connected to vibration of asymmetrical bridge Si-O-Ge which should be formed at silicon replacement by germanium. The Raman spectres of the crystals contained more than 12 weight % of GeO_2 show that the almost all absorption bands are displaced on 10-15 cm^{-1} in area of the short-wave vibration. That also can be caused by occurrence of bridge Si-O-Ge.

The data obtained on capture and distribution of germanium in quartz crystals has allowed estimating with the account of determined before piezoelectric constants for α-GeO_2 single crystals [4] possible values of the main piezoelectric constants of high-germanium quartz. They were found up to 20% higher for $Si_{0.93}Ge_{0.07}O_2$ than such of pure synthetic quartz. The electromechanical coupling coefficients of $Si_{0.93}Ge_{0.07}O_2$ are 40% higher than those of pure quartz. Thus, the study has shown that under certain hydrothermal conditions can be grown good quality crystals of high-germanium quartz. The temperature stability and piezoelectric properties of high-germanium quartz crystals are considerably over than such of pure quartz. The use of high-germanium quartz can essentially raise efficiency of piezoelectric devices.

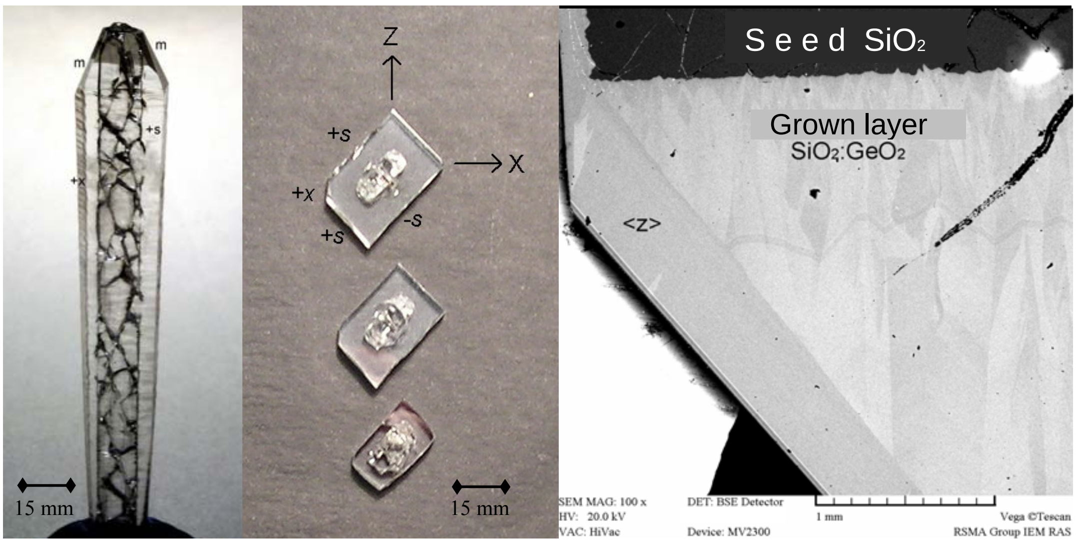

Fig.1. At the left: germanium contained quartz crystal, grown on s-seed; in the centre: cross-section cuts of the crystal; on the right: character of germanium distribution (the image in reflected electrons) in the growth sectors <z>, <c> (under the seed) and <m> (to the left of the seed)

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Electronic Scientific Information Journal "Vestnik Otdelenia nauk o Zemle RAN" № 1(27)'2009
ISSN 1819 – 6586
Informational Bulletin of the Annual Seminar of Experimental Mineralogy, Petrology and Geochemistry – 2009
URL: http://www.scgis.ru/russian/cp1251/h_dgggms/1-2009/informbul-1_2009/mineral-1e.pdf

Published on July, 1, 2009