ISSN 0012-5008, Doklady Chemistry, 2018, Vol. 481, Part 1, pp. 150–151. © Pleiades Publishing, Ltd., 2018.
Original Russian Text © G.P. Panasyuk, I.V. Kozerozhets, E.A. Semenov, V.N. Belan, M.N. Danchevskaya, A.D. Izotov, 2018, published in Doklady Akademii Nauk, 2018, Vol. 481, No. 1.

CHEMICAL TECHNOLOGY

Increasing Crystallization Rate in Growing Single Crystals of Quartz

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Received March 7, 2018

Abstract—A new method was proposed to increase the crystallization rate in growing single crystals of quartz. In this method, the crystallization is accelerated by using surfactants (polyethyleneamine, tetramethylammonium base, and polyethyleneimine) added to a soda-alkaline solution of standard concentration. Within studied ranges of pressures and concentrations of components of the solution, polyethyleneimine at a concentration of 0.002–0.05 wt % is the most efficient crystallization accelerator, which can increase the quartz crystal growth rate on the average by a factor of 2.

DOI: 10.1134/S0012500818070029

Single crystals of quartz are currently grown by a hydrothermal method, which produces crystals suitable for melting transparent quartz glass. The maximal crystal growth rate is 0.35 mm/day [1, 2].

In the hydrothermal growth of synthetic single crystals of quartz, it is always desirable to increase the crystal growth rate within accepted process conditions to increase the economic return of expensive equipment. However, single crystals produced by higher-rate methods generally have higher concentrations of impurities and, consequently, narrower ranges of application [3–5].

For example, in the hydrothermal growth of quartz crystals from soda-alkaline aqueous solutions supplemented with lead compounds (oxide, hydroxide, or carbonate) or barium compounds (hydroxide or carbonate), the crystal growth rate under standard process conditions is higher (up to 0.6–0.8 mm/day), but the range of application of the obtained single crystals is limited by elevated impurity content [3]. In particular, these crystals cannot be used for melting transparent quartz glass because of high concentrations of barium and lead impurities.

In this work, we proposed a new method to increase the rate of growth of single crystals of quartz, in which the crystallization is accelerated by using surfactants (polyethyleneamine, tetramethylammonium base, and polyethyleneimine) added to a soda-alkaline solution of standard concentration.

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The experiments were carried out in laboratory autoclaves made of 45 KhMNFA-grade steel, about 20 cm^3 in volume, at a dissolution-zone temperature of 360°C. The batch was natural gangue quartz; it was placed in a special mesh cup, which was put on the autoclave bottom. The dissolution zone was separated from the growth zone by a diaphragm with holes, the total area of which constituted about 8% of the total diaphragm area. In the upper part of the autoclave (growth zone), a frame with quartz seed plates oriented in the pinacoid plane was mounted. The temperature difference measured on the external wall of the autoclave was 20°C; the experiments lasted 14 days. The crystal growth rate was determined by measuring the change in the thickness of the crystal layer grown along the (0001) axis on one side.

The essence of the developed method is to accelerate crystallization by using surfactants. We tested such surfactants as polyethyleneamine, tetramethylammonium base, and polyethyleneimine, which were added to a soda-alkaline solution of standard concentration. The first two of the compounds had no noticeable effect on the crystallization rate, whereas polyethyleneimine $-[NH-CH_2-CH_2]_n-$ sharply increased this rate.

Table 1 shows that, within the indicated ranges of pressures and concentrations of components of the solution, polyethyleneimine at a concentration of 0.002–0.05 wt % is quite an efficient crystallization accelerator. The acceleration is maximal at a polyethyleneimine concentration of 0.005–0.02 wt %, at which the quartz crystal growth rate increases on the average by a factor of 2.

Table 1 also presents the results of quantitative chemical analysis of quartz crystals grown at different

Table 1. Results of quantitative chemical analysis of quartz crystals grown at different pressures and various concentrations of components of the solution

Solvent composition, wt %	Pressure, atm	Growth rate, mm/day	Impurity content, ppm						
			Mg	Fe	Al	Ti	Na	Ca	K
6% Na_2CO_3 + 0.5% NaOH + 0.01% PI	800	0.52	0.1	1.7	2.8	0.1	6.9	0.2	3.0
5% Na_2CO_3 + 0.5% NaOH + 0.01% PI	1000	0.56	0.1	2.1	1.5	0.1	6.5	0.2	3.0
6% Na_2CO_3 + 0.5% NaOH + 0.005% PI	1000	0.55	0.1	2.2	2.7	0.2	8.1	0.3	3.3
6% Na_2CO_3 + 0.5% NaOH + 0.01% PI	700	0.51	0.1	2.0	4.8	0.1	7.4	0.1	3.2
7% Na_2CO_3 + 0.5% NaOH + 0.005% PI	700	0.53	0.1	1.8	3.1	0.1	6.2	0.1	3.2
3% Na_2CO_3 + 0.5% NaOH + 0.01% PI	800	0.50	0.1	1.7	2.2	0.1	7.3	0.2	3.1
2% Na_2CO_3 + 0.6% NaOH + 0.01% PI	1000	0.26	Analysis was not performed						
10% Na_2CO_3 + 0.5% NaOH + 0.01% PI	1000	0.52	0.2	4.8	7.2	0.1	10.4	0.2	4.5
6% Na_2CO_3 + 0.2% NaOH + 0.005% PI	800	0.39	Analysis was not performed						
6% Na_2CO_3 + 1% NaOH + 0.005% PI	800	0.48	0.2	17.2	5.6	0.2	13.2	0.2	3.1

PI stands for polyethyleneimine. The dissolution zone temperature in all the experiments was 360°C. The temperature gradient was 20°C.

pressures and various concentrations of components of the solution.

The chemical composition was determined by dc-arc atomic emission spectroscopy with a DSF-8 diffraction spectrograph.

Thus, in this work, a new method was proposed to increase the crystallization rate in growing single crystals of quartz. In this method, the crystallization is accelerated by using surfactants. The developed method ensures much higher rate of growth of quartz crystals, the impurity content of which enables to use them for melting transparent quartz glass.

ACKNOWLEDGMENTS

This work was performed within State Assignment no. 0088–2014–0003.

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Translated by V. Glyanchenko